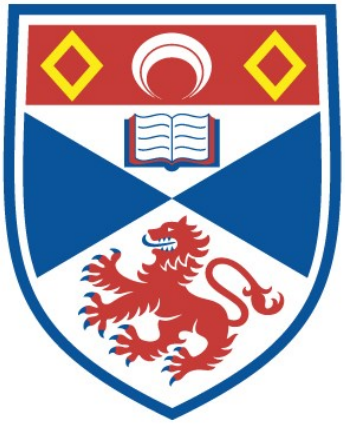
GENERATION AND REACTIVITY OF CARBON, SULPHUR AND TELLURIUM CENTRED FREE RADICALS

Peter Norman Culshaw

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1991

Generation and Reactivity of Carbon, Sulphur, and Tellurium Centred Free Radicals.

A thesis presented by Peter Norman Culshaw, BSc., to the University of St. Andrews, in application for the Degree of Doctor of Philosophy.

Declaration.

I, Peter Norman Culshaw, hereby certify that this thesis has been compiled by myself, that it is a record of my own work and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed____ _____Date 8th October 1990

I was admitted to the Faculty of Science of the University of St. Andrews, under Ordinance General No. 12 on 12th October 1987 and as a candidate for the Degree of Doctor of Philosophy on 29th September 1988

Signed___ _____Date 8th October 1990

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the Degree of Doctor of Philosophy.

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Contents

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Postgraduate Courses.

As part of the requirements of the Department of Chemistry, the following courses were attended;

Naturally Occurring Organosulphur Compounds (R.A.Aitken), Chemical Carcinogenesis (C.Thompson), Free Radicals (J.C.Walton), Cyclic Voltametry (J.A.Crayston), Heavy Atom Multiply-Bonded Compounds (R.A.Aitken), New Synthetic Methods Using Sulphur, Selenium And Phosphorous (R.K.Mackie), Free Radical Clocks (J.C.Walton), Naphthalene, Anthracene And Other Polycyclic Compounds, (D.M.G.Lloyd), Semi-conductor Growth Technology (D.J.Cole-Hamilton), Asymmetric Synthesis (R.A.Aitken).

Abbreviations.

NMR	Nuclear Magnetic Resonance
GLC	Gas-Liquid Chromatography
GC/MS	Gas Chromatography–Mass Spectrometry
ESR	Electron Spin Resonance
F.V.P.	Flash Vacuum Pyrolysis
h.f.s	Hyper-fine splitting
IR	Infra-Red
UV	Ultra-violet
δ	Relative To Tetramethylsilane
SOMO	Singly Occupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
AE	Appearance Energy
SE	Stabilisation Energy
RE	Resonance Energy
BDE	Bond Dissociation Energy
HMPT	Hexamethyl phosphoric triamide
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
AIBN	Azo-*iso*-butyronitrile
DMSO	Dimethylsulphoxide
3-t-BPD	3-*tert*-Butylpenta-1,4-diene
3-i-PPD	3-*iso*-Propylpenta-1,4-diene
Cp	Cyclopentadiene
DPPH	Diphenylpicrylhydrazyl
THF	Tetrahydrofuran
CMT	Cadmium Mercury Telluride
MOVPE	Metal Organic Vapour Phase Epitaxy

Abstract.

Using ESR dimer-radical equilibrium techniques the heat of formation, ΔH_f^o, of the pentamethylcyclopentadienyl radical was determined as 7.4 kcal mol^{-1}, and hence SE^{MeH} was calculated to be 37.9 kcal mol^{-1}. It was attempted to determine ΔH_f^o for the pentaethyl- and pentamethoxycarbonylcyclopentadienyl radicals, but this proved unsuccessful. From appearance energy measurements, ΔH_f^o (Pentadienyl) was determined to be 49.6 kcal mol^{-1}. Using photoacoustic calorimetry, the C_3–H bond dissociation energy of penta-1,4-diene and several 3-substituted pentadienes were determined; *i.e.* for penta-1,4-diene ($DH^o(C_3–H)$ = 76.4±0.6 kcal mol^{-1}), 3-methyl-penta-1,4-diene ($DH^o(C_3–H)$ = 76.6±0.6 kcal mol^{-1}) and 3-hydroxypenta-1,4-diene ($DH^o(C_3–H)$ = 69.0±0.6 kcal mol^{-1}). ESR exchange broadening methods were used to show that SE^{ESR} (3-methylpentadienyl) is virtually the same as that of the parent pentadienyl radical, (*i.e.* 25 kcal mol^{-1}). The 3-hydroxypentadienyl, 1-hydroxy-3-methylpentadienyl and 1-trimethylsilyloxy-3-methylpentadienyl radicals were generated, but exchange broadening was not observed in the accessible temperature range.

Sulphonate esters were examined as a potential source of free radicals. The reaction of simple alkyl alkanesulphonates with photochemically generated trimethyltin radicals in the cavity of an ESR spectrometer gave the corresponding alkane sulphonyl radicals. Good ESR spectra were obtained when sulphonyl radicals, generated from sulphonate esters, were used to form adduct radicals with alkenes of the type CH_2=CHR, where R is an electron releasing substituent, (R = OMe, OBu^n, SPh, $SiMe_3$). Delocalised radicals were generated from sulphonate esters which contained a terminal alkenyl or alkynyl substituent. For example, the reaction of allyl methanesulphonate with photochemically generated trimethyltin radicals in the cavity of an ESR spectrometer gave good spectra of the allyl radical.

The pent-4-ene-1-sulphonyl radical was generated from the corresponding sulphonyl chloride using several different radical initiator systems (tri-*n*-butyltin hydride, triphenylsilane, hexa-*n*-butylditin, 9-trimethylstannyl-9,10-dihydroanthracene, copper (II) chloride and tris (triphenylphosphine) ruthenium (II) chloride). The radical was found to cyclise in a predominantly *endo*-fashion to give 3-chlorotetrahydrothiopyran-1,1-dioxide, the exact proportion of *endo*- and *exo*-products depending on the temperature. The hex-5-ene-1-sulphonyl radical was found to give thiepane-1,1-dioxide, also the product of *endo*-cyclisation. The inclusion of a bulky ring substituent forced the cyclohexenylethanesulphonyl radical to cyclise in the *exo*-mode to give 2-chloro-9-thiabicyclo[4.3.0]nonane-9,9-dioxide.

Dialkyltellurides and dialkylditellurides gave the corresponding alkyl radical on photolysis in the cavity of an ESR spectrometer. For example, diallyltelluride gave good spectra of the allyl radical. Under thermolysis conditions, a nitrosodurene spin trap was employed to observe the trapped alkyl radicals. It is believed that certain of the trapped radicals were tellurium-centred species.

To My Parents

"The first principle is that you must not fool yourself - and you are the easiest person to fool. So you have to be very careful about that. After you've not fooled yourself, it's easy not to fool other scientists. You just have to be honest in a conventional way after that."

"Surely You're Joking Mr. Feynman"
R.P.Feynman

Part One

Carbon Centred Free Radicals

Chapter One

Introduction To Radical Stabilisation Energy.

1.1 Delocalisation, Resonance And Conjugation.

Bond formation between two atoms may be envisaged as the progressive overlapping of the atomic orbitals of the two participating atoms; the greater the amount of orbital overlap, the stronger the resultant bond is. The combination of two carbon atoms, for example in ethane, results from the axial overlap of two sp^3 hybrid orbitals, one from each carbon atom, to form a strong σ bond between them. The bonding between compounds of this type can be described by a single Lewis structure, but this is not sufficient for many other compounds. Bonding in compounds in which one or more of the bonding orbitals is not restricted to two atoms but is spread out over three or more is said to be delocalised.

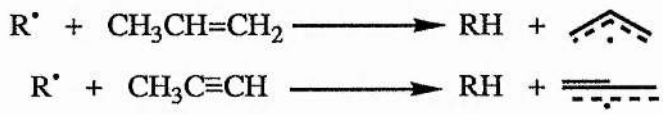
Molecules which exhibit delocalisation may be represented by several possible Lewis structures (known as canonical forms); the molecule being taken as a weighted average between these forms. The representation of molecular structures as a weighted average of two or more canonical forms is known as resonance, the effect of which can markedly increase the stability of a molecule, (for example the benzene molecule). Resonance stabilisation, which is well known for cyclic systems such as benzene, is also possible in acyclic systems such as conjugated dienes and polyenes.

In compounds that contain more than one multiple bond, for example dienes with two C=C bonds, it is found that if the bonds are conjugated (that is, alternating multiple and single) then these molecules are slightly more stable than those with isolated double bonds. The additional thermodynamic stability of conjugated compounds is reflected in their having both lower heats of combustion and hydrogenation, and also in the observation that non-conjugated systems often readily undergo bond migration to the corresponding conjugated isomers.

In cases where the molecule contains an odd number of π-electrons the resulting species is a free radical. Free radicals with electron delocalisation are often preferentially formed from alkenes, alkynes, dienes and polyenes because of their extra stabilisation.

1.2 Formation Of Delocalised Radicals.

Hydrogen abstraction from alkenes or alkynes is the most commonly used route to delocalised radical formation.



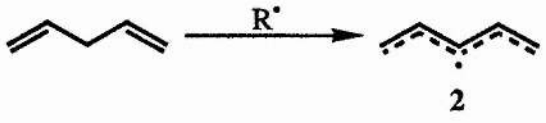
The nature of the primary radical, R•, which may be generated by thermal or photochemical means, is important because hydrogen abstraction often competes with the addition reaction, namely;

Thus, R• is often hydroxyl, alkylperoxyl or, the most commonly used *tert*-butoxyl, for which in each case hydrogen abstraction is the favoured route. However, in the case of conjugated dienes, *e.g.* buta-1,3-diene, addition may occur more readily than hydrogen abstraction.

1

The driving force for this addition reaction is the formation of a stabilised substituted allyl radical, **1**.

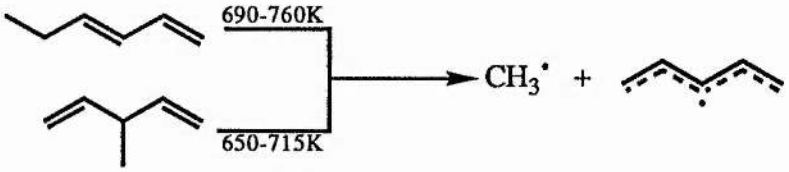
Hydrogen abstraction also occurs very readily from bis-allylic methylenic groups in 'skipped' dienes such as penta-1,4-diene to give the pentadienyl radical, **2**.



2

In this case, delocalisation of the unpaired electron now extends over five carbon atoms, thereby increasing the radical stability.

Delocalised radicals are also formed by homolytic fission in alkenes and polyenes, either by UV irradiation or pyrolysis, *e.g.* pyrolysis of hexa-1,3-diene[1] or 3-methylpenta-1,4-diene.[2]



Halogen abstraction from haloalkenes or haloalkynes is usually the preferred mode of generating delocalised radicals for ESR study. Halogen abstraction may be carried out using photochemically generated trialkylsilyl[3] or trialkyltin radicals.[4]

$$^tBuOOBu^t \xrightarrow{h\upsilon} 2\,^tBuO^{\bullet}$$

$$^tBuO^{\bullet} + R_3MH \longrightarrow R_3M^{\bullet} + {}^tBuOH$$

$$R_3M^{\bullet} + XCH_2CH{=}CH_2 \longrightarrow R_3MX + \dot{C}H_2{-}\dot{C}H{-}CH_2$$

Allyl and analogous radicals are thermodynamically stabilised by electron delocalisation but this does not mean that they are kinetically stable. Hence, allyl and propynyl radicals are as reactive as primary alkyl radicals and their lifetimes are of a similar order. Allyl radicals have been shown to abstract hydrogen from toluene very rapidly, which led to the conclusion that they behave much more 'normally' (*i.e.* like

alkyl radicals) than was thought to be the case previously, and their resonance stabilisation has little effect on their rates of reaction with other radicals.[5]

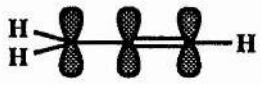
Such radicals can be made persistent by suitably positioned bulky substituents (*e.g.* *tert*-Bu or R_3Si) the large size of which sterically impedes the approach of one radical centre to another. Such radicals often have relatively long lifetimes, *e.g.* 1,1-di-*tert*-butylbenzyl radical (stable for several days at room temperature)[6] and 1,1-di-*tert*-butyl-2-methylallyl.[7]

The bent structure of the allyl skeleton enables it to exist as two possible stereoisomers; the *anti*-conformer, **3**, and the *syn*-conformer, **4**.

3 **4**

Both of these conformers have been distinguished by ESR for many types of substituent, X.[8] Conversion of one conformer to the other requires rotation about the C_1–C_2 partial double bond, but the energy barrier to rotation is too high for this to be observed by ESR within the accessible temperature range. For the majority of substituents the energy barrier is sufficiently high that retention of configuration is attained, however, certain substituents such as *tert*-Bu, CN and F lower the barrier and interconversion is observable.

The propynyl radical is also readily observable by ESR but, unlike the allyl radical, it only exists as a single π-delocalised structure, **5**,



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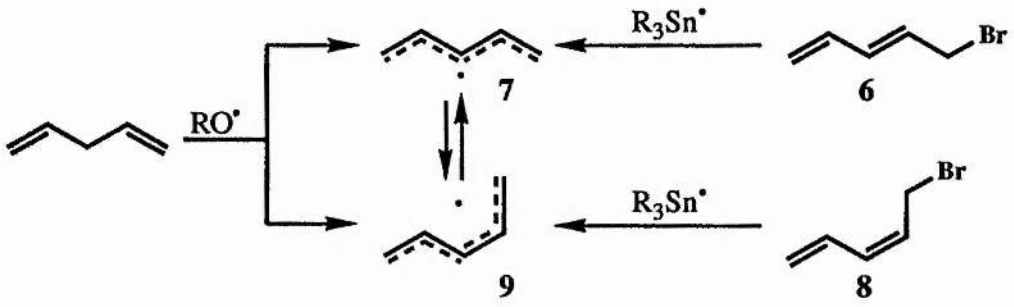
in which the main centre of unpaired electron density is the sp^2 hybridised carbon.[9]

Pentadienyl radicals have been observed spectroscopically by ESR by hydrogen abstraction from penta-1,4-diene[10-12] or bromine abstraction using trialkyltin radicals[13] from *cis*- and *trans*-5-bromopenta-1,3-diene.



The *trans*-bromide, **6**, gave the *W*- or *E,E*-conformation, **7**, and this was the only radical observed in the temperature range 143-450 K. Bromine abstraction from the *cis*-bromide, **8**, gave the *Z*- or *E,Z*-conformation, **9**, but at temperatures >160 K this was found to isomerise by rotation of the C_2–C_3 partial double bond till at T >210 K only the *W*-conformer remained.

Penta-1,4-diene exists in three conformers and hence hydrogen abstraction leads to both *W*- and *Z*-conformers. The third possible conformer the *U*- or *Z,Z*-, **10**, has not been observed.

10

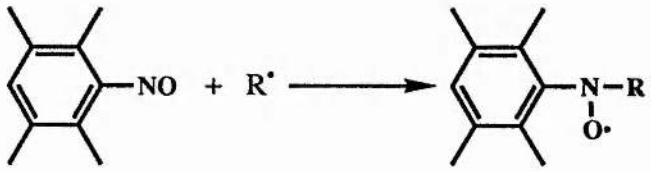
1.3 Cyclic Radicals.

Data on the stabilisation of cycloalkenyl radicals are scarce, and are mainly limited to the cyclohexenyl radical.[14,15] Other cyclic systems for which ΔH_f^o has been derived include the cyclopropenyl[16], cyclopentadienyl[17] and cycloheptatrienyl radicals.[18] Polycyclic aromatic hydrocarbon radicals have also been investigated.[19] The additional π-bonding stabilisation energy of such molecules increases the overall stability of the radical.

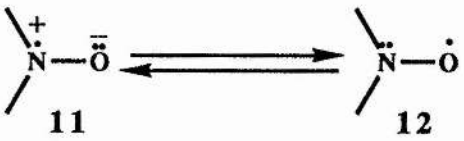
1.4 Spin Trapping.

Another class of radicals which are highly stable are the nitroxides. These are so stable as to be called 'persistent' and they can be stored for several months or years under the right conditions.

The use of nitroso compounds as spin traps is an important area in ESR spectroscopy. Occasionally very transient radicals whose lifetimes are too short to be observed, or radicals which are below the detection limit can be 'trapped' using such nitroso compounds to form nitroxide adduct radicals which are persistent, and allow the nature of the trapped radical to be determined. One of the most commonly used spin traps is nitrosodurene[20] which reacts with most carbon-centred free radicals as shown:



The N–O group contains one unpaired electron and the structure of this group can be seen as a superposition of two mesomeric structures.[21]



11 **12**

The contribution of the first or second structure to the ground state may be different, depending on the effects of conjugation and polarity of the medium. The resonance hybrid formulation of **11** and **12** indicates the unique stabilisation of these radicals in which three π-electrons are distributed over two atomic centres.[22]

1.5 Stabilisation Energy.

Alkenyl and polyenyl radicals are thermodynamically stabilised by delocalisation of the unpaired electron over the double bonds. The resonance energy (RE) or stabilisation energy (SE) of such radicals ($R^{\bullet}$) is defined as the difference between the C–H bond dissociation energy in RH and the C–H bond dissociation energy in a non-resonating model compound, MH.

$$SE^{MH} = DH^{o}(MH) - DH^{o}(RH)$$
$$= [\Delta H_f^{o}(M^{\bullet}) - \Delta H_f^{o}(MH)] - [\Delta H_f^{o}(R^{\bullet}) - \Delta H_f^{o}(RH)]$$

For odd conjugated systems, the choice of a non-resonating model compound is not always easy. Estimation of alkenyl radical resonance energies by comparison of primary or secondary radicals has been used.[1,2,23] However, the primary and secondary radicals themselves are strongly stabilised by hyperconjugative and inductive effects, and whilst allyl, pentadienyl and other polyenyl radicals are also stabilised by hyperconjugative/inductive effects, it is to a much lesser extent because they have fewer β hydrogens than the model compounds. Thus, stabilisation energies derived on this basis probably over-compensate for the hyperconjugative/inductive contribution and hence underestimate the actual resonance energy.

Stabilisation energy of odd conjugated radicals relative to methyl radicals[13,24] would give a methane based stabilisation energy.

$$SE^{MeH}(R^{\bullet}) = DH^{o}(CH_3\text{–}H) - DH^{o}(R\text{–}H)$$

Use of methane as a model compound is desirable because;

(i) Use of a single reference compound with a well established bond dissociation energy will introduce uniformity into the data .

(ii) The methyl radical is not stabilised by hyperconjugative/inductive effects.

This means, however, that SE values obtained contain contributions from both electron delocalisation and hyperconjugative/inductive stabilisation and hence such values will be greater than other SE^{MH} values. SE^{MeH} values will not give an accurate measure of resonance stabilisation unless hyperconjugative/inductive and other stabilising factors are negligible.

1.6 Determination Of Stabilisation Energy.

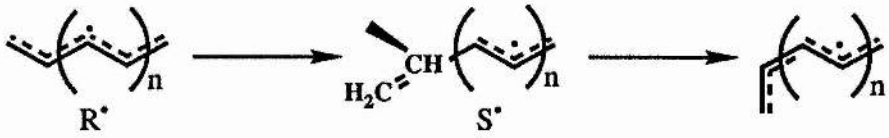
As stabilisation energy is directly related to bond dissociation energy, techniques which can be used to derive this latter parameter can be used to derive SE data.

Heats of formation of free radicals and hence homolytic bond dissociation energies are difficult to measure to an adequate level of accuracy, due to experimental difficulties and the fact that free radicals are generally transient intermediates, both in solution and the gas phase and hence are inappropriate subjects for conventional calorimetry.[25]

1.7 Electron Spin Resonance Methods.

1.7.1 Energy Barrier To Rotation.

Internal rotation of 90° about the C_2–C_3 bond of a polyenyl radical results in the stabilisation due to delocalisation in the end vinyl group being lost. The radical effectively becomes a polyenyl radical two carbon atoms shorter with a vinyl substituent. Thus, for *trans/trans-* to *cis/trans*-interconversion we have;



The activation energy, E_i, for the above isomerisation is related to stabilisation of the initial polyenyl radical, R•, and the stabilisation energy of the vinyl substituted radical, S•, by the equation;

$$E_i = V_2 + SE^{ESR}(R^\bullet) - SE^{ESR}(S^\bullet)$$

where V_2 is the barrier to rotation about the single C_2–C_3 bond in the absence of delocalisation.

Rotational barrier methods have been used to determine the stabilisation energies of substituted allyl,[26-28] pentadienyl, pent-2-en-4-ynyl[29] and heptatrienyl[30] radicals.

1.7.2 Radical Buffers.

The exchange reaction between alkyl radicals and alkyl iodides is a rapid process.[31-33]

$$R^\bullet + R'I \underset{}{\overset{K}{\rightleftharpoons}} RI + R'^\bullet$$

Under the right conditions, this exchange can be more rapid than radical-radical reactions (*e.g.* R•, R'• combination to give R–R'). Using ESR it has been shown that the equilibrium constant of the reaction can be measured,[34] which enables the BDE and hence the SE to be obtained.

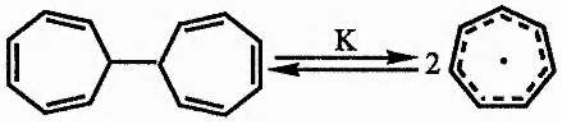
However, whilst this technique enables relative heats of formation to be determined for simple alkyl radicals it is of no use with highly stabilised radicals such as allyl or benzyl. Such radicals abstract iodine from alkyl iodides insufficiently fast to ensure that the buffer reaction is very much faster than the radical-radical processes.

1.7.3 Dimer-Radical Equilibrium.

A technique not unlike the radical buffer method, involving the equilibrium between the radical of interest and its corresponding dimer, has been developed.

$$R_2 \underset{}{\overset{K}{\rightleftharpoons}} 2R^{\bullet}$$

This method has been used to determine the heat of formation of the cycloheptatrienyl radical, **13**, from the dimer bis(cyclohepta-2,4-6-trien-1-yl).[18]



13

The homolytic thermal cleavage of neat liquid bis(cyclohepta-2,4,6-trien-1-yl) was investigated by ESR. The equilibrium constant, K, was derived using the relative concentration of R• observed by ESR and the density of the dimer at each temperature studied.

An adaptation of this method has been used in this work to derive the stabilisation energy of substituted cyclopentadienyl radicals.

1.8 Mass Spectrometry.

The appearance energy technique makes use of an energy resolved electron beam to cleave a molecule in the gas phase to an ion and a radical.

$$R\text{-}R' + e^- \xrightarrow{AE} R^+ + R'^{\bullet} + 2e^-$$

The ions were detected in a quadrupole mass spectrometer. In a typical experiment, the electron energy is slowly increased until a current due to the desired ion is detected. The appearance energy is related to the heat of formation of the radical. This

technique has been used in this work to determine ΔH_f^o for pentadienyl radicals, (see § 2.5 and references therein).

1.9 Photoacoustic Calorimetry.

Measurements of the strength of weak carbon-hydrogen bonds, or those in organometallic or high molecular weight compounds have presented severe experimental difficulties because of the limitations of gas phase techniques. The photoacoustic method provides a practical alternative to the problem. The technique has been used in this work to determine the C_3–H bond dissociation energy for penta-1,4-diene and several other 3-substituted penta-1,4-dienes (see § 2.7.and references therein).

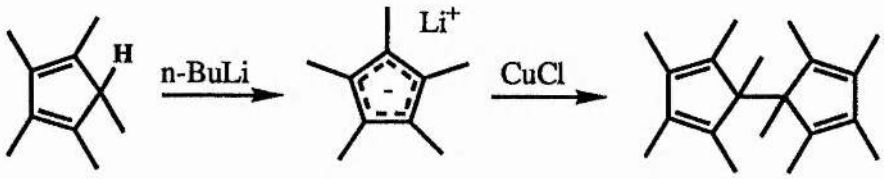
Chapter Two

Stabilisation Energies Of Delocalised Free Radicals.

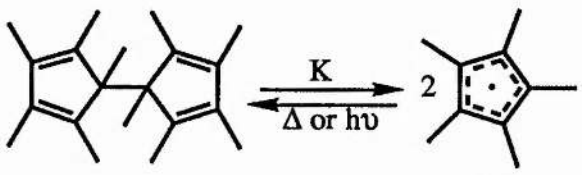
Stabilisation energies of delocalised free radicals are of great importance in thermochemical and kinetic modelling of free radical processes. The derivation of SEs and related thermodynamic parameters, such as radical heats of formation and hydrocarbon bond dissociation energies of cyclopentadienyl and pentadienyl radicals, has been investigated.

2.1 Determination Of The Stabilisation Energy Of The Pentamethyl-cyclopentadienyl Radical.

The pentamethylcyclopentadienyl radical, **1**, was generated in the cavity of an ESR spectrometer by thermolysis of a solution of the corresponding dimer, 1,1',2,2',3,3',4,4',5,5'-decamethyl-bis(cyclopentadienyl)[35], which was prepared from 1,2,3,4,5-pentamethylcyclopenta-1,3-diene using *n*-butyl lithium and freshly prepared copper (I) chloride[36] as outlined below;



This dimer has been shown to undergo homolytic cleavage under photolysis conditions to give the pentamethylcyclopentadienyl radical.[37]



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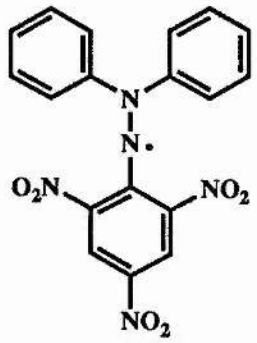
In order to determine the stabilisation energy, the equilibrium constant, K, is required over a range of temperatures, which in turn may be determined from the concentration of the pentamethylcyclopentadienyl radical from a solution of known dimer concentration over that temperature range.

It has been reported that dimer-radical equilibrium techniques can be used to determine the stabilisation energy of the cycloheptatrienyl radical using a modified version of the van't Hoff equation, using solution density and several other terms to replace the equilibrium constant.[18]

The ESR spectrum of the pentamethylcyclopentadienyl radical (a(15H) 6.4 G, Lit.[37] 6.4 G; Figure 1) consists of 16 lines, due to the 15 equivalent protons of the five methyl groups. The line chosen for study was the second most intense, which, on the basis of the binomial expansion $(x+1)^{15}$, has a relative intensity of 5005/32768. Samples of known dimer concentration were prepared in *n*-hexadecane and degassed before thermolysis. The pentamethylcyclopentadienyl radical was first observed at 359 K. The radical concentration remained relatively constant over the time of observation at each temperature, up to *ca.* 376 K, but above this temperature, the radical concentration was observed to fall over a period of time. At temperatures of 382-393 K, the radical concentration was measured at timed intervals and extrapolated back to determine the initial radical concentration at these temperatures. As ESR spectra are normally recorded as first derivative, the peak under study (5005/32876) was converted to its absorption spectrum and the 'area' under the peak was determined at each temperature. The 'areas' were relative and were determined by weighing each peak. Calibration was achieved by measuring the response due to a solution of known radical concentration. A 10^{-3} M solution of the stable radical diphenylpicrylhydrazyl, (DPPH), **2**,



2

was analysed by ESR and its derivative spectrum and hence its 'area' was determined. The signal due to a ruby crystal was also measured at each temperature to act as a standard over any daily instrument fluctuations. The radical concentration [R•] was determined at each temperature using the equation:

$$[R^{\cdot}] = [DPPH] \times \frac{Wt_R}{Wt_{DPPH}} \times \frac{Gain_{DPPH}}{Gain_R} \times \frac{(\Delta H_R)^2}{(\Delta H_{DPPH})^2} \times \frac{Ruby_{DPPH}}{Ruby_R} \times \frac{T_R}{T_{DPPH}} \times F$$

[R•] = Radical Concentration.

Wt_R, Wt_{DPPH} = Weight of paper under the area of the curve for the derivative spectrum of the radical (R) or diphenylpicrylhydrazyl (DPPH).

$Gain_R$, $Gain_{DPPH}$ = Gain setting on ESR spectrometer used for recording the signal of the radical (R) or diphenylpicrylhydrazyl (DPPH).

ΔH_R, ΔH_{DPPH} = Magnetic field increments in which the derivative spectrum was converted to its absorption spectrum.

$Ruby_R$, $Ruby_{DPPH}$ = Size of ruby signal at each temperature the radical (R) and diphenylpicrylhydrazyl (DPPH) was studied.

T_R, T_{DPPH} = Temperature at which the radical (R) or diphenylpicrylhydrazyl (DPPH) signal was recorded.

F = Proportion of peak studied compared to whole spectrum

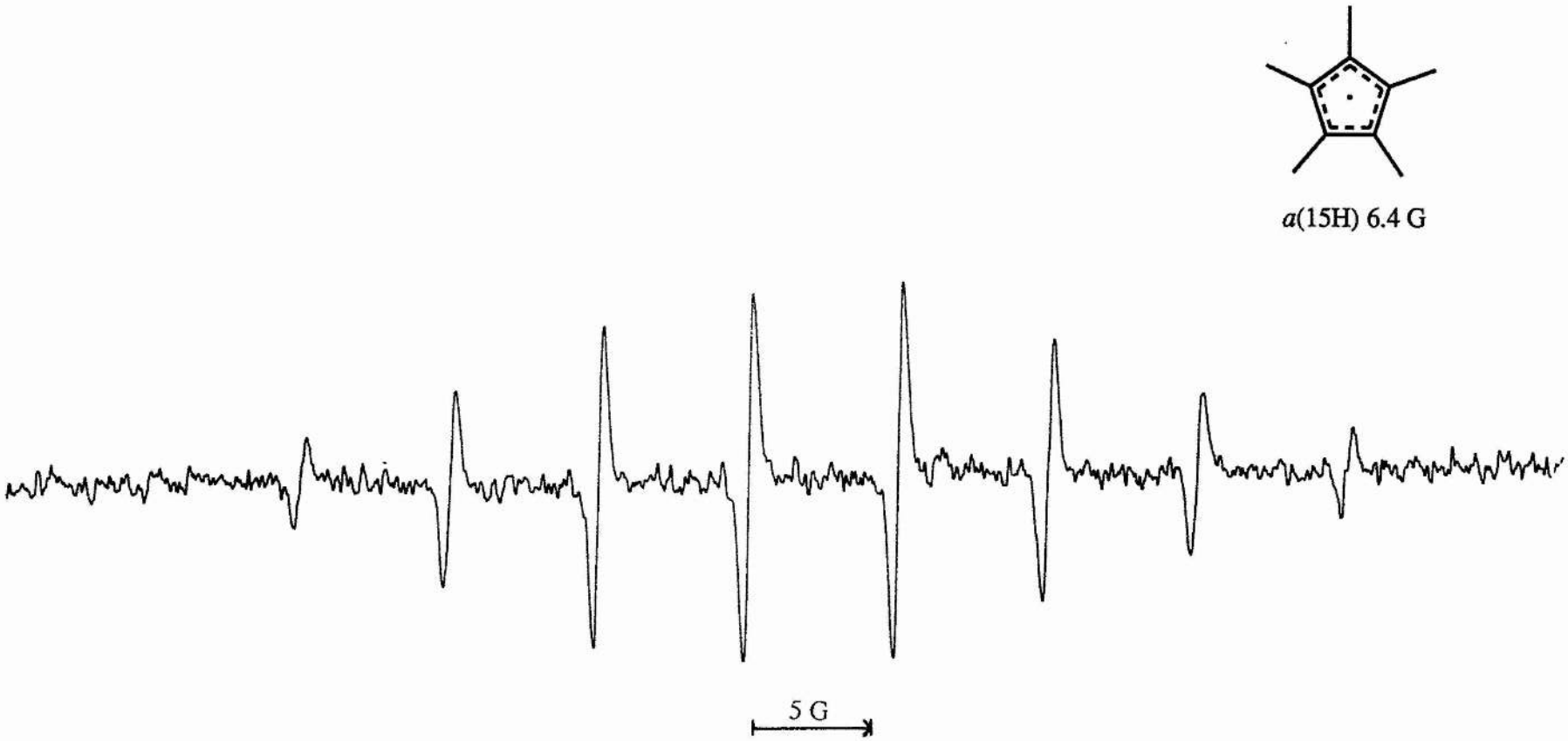


Figure 1. ESR Spectrum Of The Pentamethylcyclopentadienyl Radical.

Determination of reaction enthalpy is from the van't Hoff isochore (1):

$$d\ln K/dT = \Delta H_m^o(T)/RT^2 \qquad (1)$$

now, $(d/dT)(1/T) = 1/T^2$ or $dT/T^2 = -d(1/T)$

which means the isochore can be re-written as:

$$d\ln K/d(1/T) = -\Delta H_m^o(T)/R \qquad (2)$$

which in turn can be re-written as:

$$2.303\log K = -\Delta H_m^o(T)/RT \qquad (3)$$

From (3), a plot of logK *versus* $10^3/T$ should give a straight line.

$$\text{gradient} = (-\Delta H_m^o)/2.303R$$

$$-\Delta H_m^o = \text{gradient} \times 2.303R$$

The data obtained are tabulated below;

T (K)	Av. Weight (g)	Gain	Ruby (mm)	[R•] mol dm^{-3}
365	0.8294	1.60×10^6	142	3.508×10^{-8}
371	0.9480	1.60×10^6	140	4.134×10^{-8}
376	1.2172	1.60×10^6	152	4.955×10^{-8}
382	1.1168	1.25×10^6	150	5.991×10^{-8}
388	1.1533	1.25×10^6	128	7.364×10^{-8}

At higher temperatures the rate of decay of the dimer increased to such a point that errors due to irreversible side reactions would occur. Thus, the radical concentration at high temperatures was recorded over a period of time, and concentration was extrapolated back to time = zero, before the dimer-radical equilibrium breaks down.

T = 382 K; Gain = 8 x 10^5; Ruby = 157 mm

Time (s)	Weight (g)	[R•] mol dm^{-3}	$\log_{10}$[R•]
50	0.8293	6.641 x 10^{-8}	-7.18
127	0.8293	6.641 x 10^{-8}	-7.18
252	0.7472	5.984 x 10^{-8}	-7.22
410	0.7335	5.874 x 10^{-8}	-7.23
453	0.7062	5.655 x 10^{-8}	-7.25
624	0.6925	5.546 x 10^{-8}	-7.26
1020	0.6377	5.107 x 10^{-8}	-7.29

Plot $\log_{10}$[R•] *versus* time

At time = 0, $\log_{10}$[R•] = -7.18

$[R^{\bullet}]_{382K}$ = 6.607 x 10^{-8} mol dm^{-3}.

T = 388 K; Gain = 6.3 x 10^5; Ruby = 157 mm

Time (s)	Weight (g)	[R•] mol dm^{-3}	$\log_{10}$[R•]
105	1.2674	1.309 x 10^{-7}	-6.88
164	1.1168	1.154 x 10^{-7}	-6.94
263	0.9799	1.012 x 10^{-7}	-6.99
431	0.8978	9.274 x 10^{-8}	-7.03
614	0.7198	7.436 x 10^{-8}	-7.13
732	0.6103	6.304 x 10^{-8}	-7.20
965	0.4461	4.608 x 10^{-8}	-7.34
1170	0.3092	3.194 x 10^{-8}	-7.50

Plot $\log_{10}$[R•] *versus* time

At time = 0, $\log_{10}$[R•] = -6.82

$[R^{\bullet}]_{388K}$ = 1.514 x 10^{-7} mol dm^{-3}.

T = 393 K; Gain = 10.0 x 10^5; Ruby = 152 mm

Time (s)	Weight (g)	[R·] mol dm^{-3}	$\log_{10}$[R·]
92	2.3488	1.599 x 10^{-7}	-6.80
155	1.8834	1.282 x 10^{-7}	-6.89
216	1.8012	1.226 x 10^{-7}	-6.91
315	1.4864	1.012 x 10^{-7}	-6.99
430	1.1579	7.882 x 10^{-8}	-7.10
488	1.0484	7.136 x 10^{-8}	-7.15
613	0.8020	5.459 x 10^{-8}	-7.26

Plot $\log_{10}$[R•] *versus* time

At time = 0, $\log_{10}$[R•] = -6.73

$[R^{\bullet}]_{393K}$ = 1.862 x 10^{-7} mol dm^{-3}.

The equilibrium constant, $K = [R^{\bullet}]^2/[R_2]$ at each temperature studied was required, and $[R_2]$ at each particular temperature was calculated using the equation;

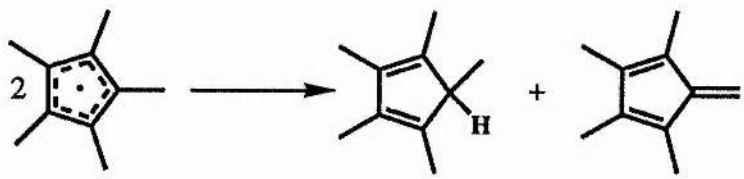
$$[R_2] = [R_{2\ Init.}] - 2[R^{\bullet}]$$

The following table shows a summary of the data obtained for the experiment;

T(K)	$[R^{\bullet}]$ mol dm^{-3}	$[R_{2\ Init.}]$ mmol dm^{-3}	K	$10^3/T$	$\log_{10}K$
365	3.508×10^{-8}	48.99	2.512×10^{-14}	2.74	-13.60
371	4.134×10^{-8}	48.99	3.488×10^{-14}	2.70	-13.46
376	4.955×10^{-8}	48.99	5.012×10^{-14}	2.66	-13.30
382	5.991×10^{-8}	48.99	7.326×10^{-14}	2.62	-13.14
388	7.364×10^{-8}	48.99	1.107×10^{-13}	2.58	-12.96
Extrapolated data					
382	6.607×10^{-8}	53.61	8.124×10^{-14}	2.62	-13.09
388	1.514×10^{-7}	52.69	4.351×10^{-13}	2.58	-12.36
393	1.862×10^{-7}	52.69	4.768×10^{-13}	2.54	-12.32

From these data a graph of $10^3/T$ *versus* $\log_{10}K$ was plotted and the gradient was determined.

Data points at very high temperature or temperatures at which the radical is only just beginning to form did not fit very well on the line. Deviation of the points at higher temperatures is probably due to an irreversible side reaction becoming predominant over the dimer-radical equilibrium. It has been reported that apart from recombination of the cyclopentadienyl radical to give the dimer, irreversible disproportionation to give the parent cyclopentadiene and tetramethylfulvalene, **3**, may occur.[37]



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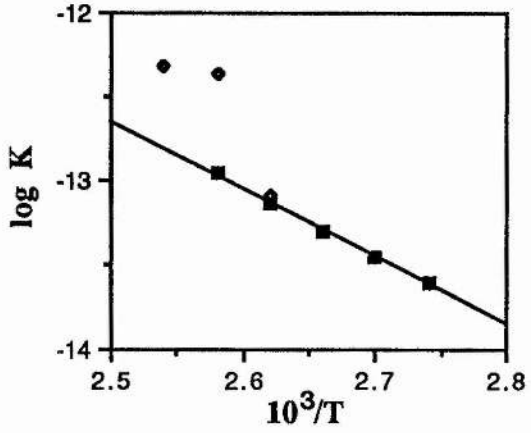
Tetramethylfulvalene is yellow, and solutions of the heated dimer were found to have become bright yellow after prolonged heating at high temperatures. Therefore,

only the data obtained over the linear region of the plot were used to determine the gradient,



which was found to be -4.111

Hence; $-\Delta H_m^o = -4.111 \times 2.303 \times 1.98720$

$\Delta H_m^o = \underline{18.81}$ kcal mol^{-1}

2.1.1 Calculation Of Stabilisation Energy.

The heats of formation for dimer and monomer were calculated from the Benson group equivalents.[23] However, there are no Benson group equivalents for $[C–(C_d)_2(C)(H)]$, $[C–(H)_3(C_d)]$ or $[C–(C_d)_2(C)_2]$.

These can be estimated as follows;

The difference between $[C–(C)_4]$ and $[C–(C_d)(C)_3]$ is one C_d which is 1.18 kcal mol^{-1}. The difference between $[C–(C_d)(C)_3]$ and $[C–(C_d)_2(C)_2]$ is also one C_d and so $[C–(C_d)_2(C)_2] = 1.68 + 1.18 = 3.86$ kcal mol^{-1}.

The difference between $[C–(C_d)(C)(H)_2]$ and $[C–(C)_2(H)_2]$ which is one C_d is 0.17 kcal mol^{-1}. The difference between $[C–(C_d)(H)_3]$ and $[C–(C)(H)_3]$ is also one C_d, assuming the same difference as before, then as $[C–(C)(H)_3]$ is -10.20 kcal mol^{-1} we get $[C–(C_d)(H)_3] = (-10.20) – (-0.17) = -10.03$ kcal mol^{-1}.

These derived group values were used to estimate ΔH_f^o(Dimer), $\Delta H_f^o(CpMe_5^\bullet)$ and $\Delta H_f^o(CpMe_5H)$.

<u>ΔH_f^o(Dimer)</u>

$\Delta H_f^o(Cp_2Me_{10}) = 2([C-(C_d)_2(C)_2] + 2[C_d-(C)_2] + 2[C_d-(C_d)(C)] + [C-(H)_3(C)] +$
$4[C-(H)_3(C_d)] + \text{ring contribution})$
$= 2[(3.86) + 2(10.34) + 2(8.88) + (-10.20) + 4(-10.03) + (6.0)]$

$\Delta H_f^o(Cp_2Me_{10}) = -4.04$ kcal mol^{-1}.

<u>$\Delta H_f^o(CpMe_5^\bullet)$</u>

$\Delta H_m^o = 2\Delta H_f^o(CpMe_5^\bullet) - \Delta H_f^o(Cp_2Me_{10})$

$18.81 = 2\Delta H_f^o(CpMe_5^\bullet) - (-4.04)$

$\Delta H_f^o(CpMe_5^\bullet) = 7.39$ kcal mol^{-1}.

<u>$\Delta H_f^o(CpMe_5H)$</u>

$\Delta H_f^o(CpMe_5H) = ([C-(C_d)_2(C)(H)] + 2[C_d-(C)_2] + 2[C_d-(C_d)(C)] + [C-(H)_3(C)] +$
$4[C-(H)_3(C_d)] + \text{ring contribution})$
$= [(-1.0) + 2(10.34) + 2(8.88) + (-10.20) + 4(-10.03) + (6.0)]$

$\Delta H_f^o(CpMe_5H) = -6.88$ kcal mol^{-1}.

The stabilisation energy of a radical relative to a model compound MH, may be defined as

$SE^{MH} = [\Delta H_f^o(M^\bullet) - \Delta H_f^o(MH)] - [\Delta H_f^o(R^\bullet) - \Delta H_f^o(RH)]$

Relative to methane, the SE is

$SE^{MeH} = [\Delta H_f^o(CH_3^\bullet) - \Delta H_f^o(CH_4)] - [\Delta H_f^o(CpMe_5^\bullet) - \Delta H_f^o(CpMe_5H)]$
$= [34.4 - (-17.8)] - [7.39 - (-6.88)]$
$SE^{MeH} = 37.93$ kcal mol^{-1}.

Relative to *iso*-butane, the SE is

$$SE^{t\text{-}BuH} = [\Delta H_f^o(^tBu^\bullet) - \Delta H_f^o(^tBuH)] - [\Delta H_f^o(CpMe_5^\bullet) - \Delta H^o\ (CpMe_5H)]$$

$$= [9.4 - (-32.1)] - [7.39 - (-6.88)]$$

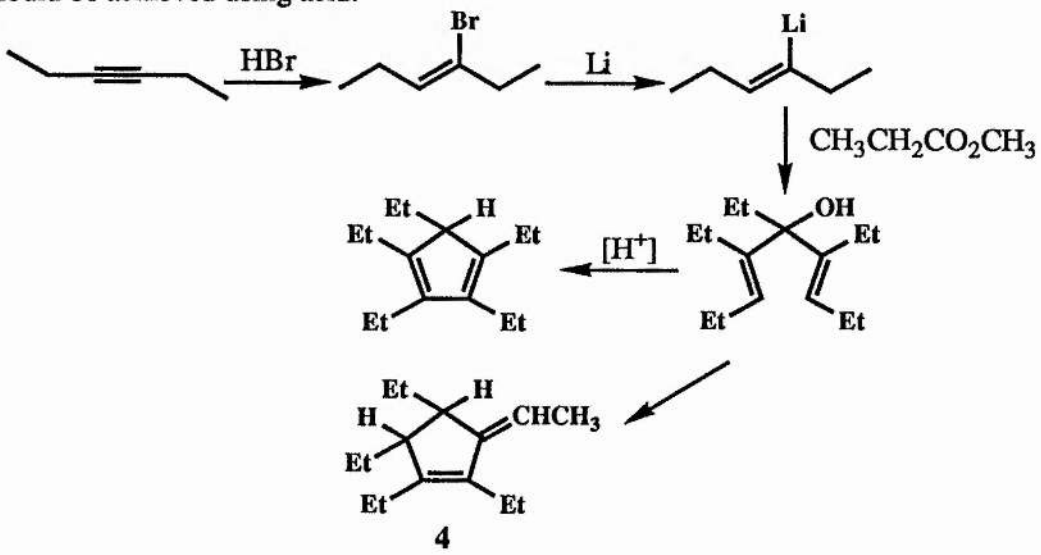
$$SE^{t\text{-}BuH} = 27.23 \text{ kcal mol}^{-1}.$$

Comparison of the stabilisation energy of the pentamethylcyclopentadienyl radical with other carbon centred radicals shows that the effect of π-delocalisation in cyclic alkenes significantly enhances the radical stability, (see § 2.9).

2.2 Decaethylbiscyclopentadiene.

It was decided to prepare the decaethyl analogue to determine the stabilisation energy of the pentaethylcyclopentadienyl radical. Whilst there are many literature references to organometallic compounds containing the pentaethylcyclopentadiene ring as a ligand, the isolated monomer itself has not previously been reported. It was decided to prepare the compound by a method analogous to that used to prepare the pentamethyl compound.[38]

3-Bromohex-3-ene was prepared by bubbling HBr gas through hex-3-yne.[39] The bromide was then lithiated using lithium wire and reacted with methyl propionate, to form the intermediate alkenol. Elimination of water and subsequent cyclisation should be achieved using acid.



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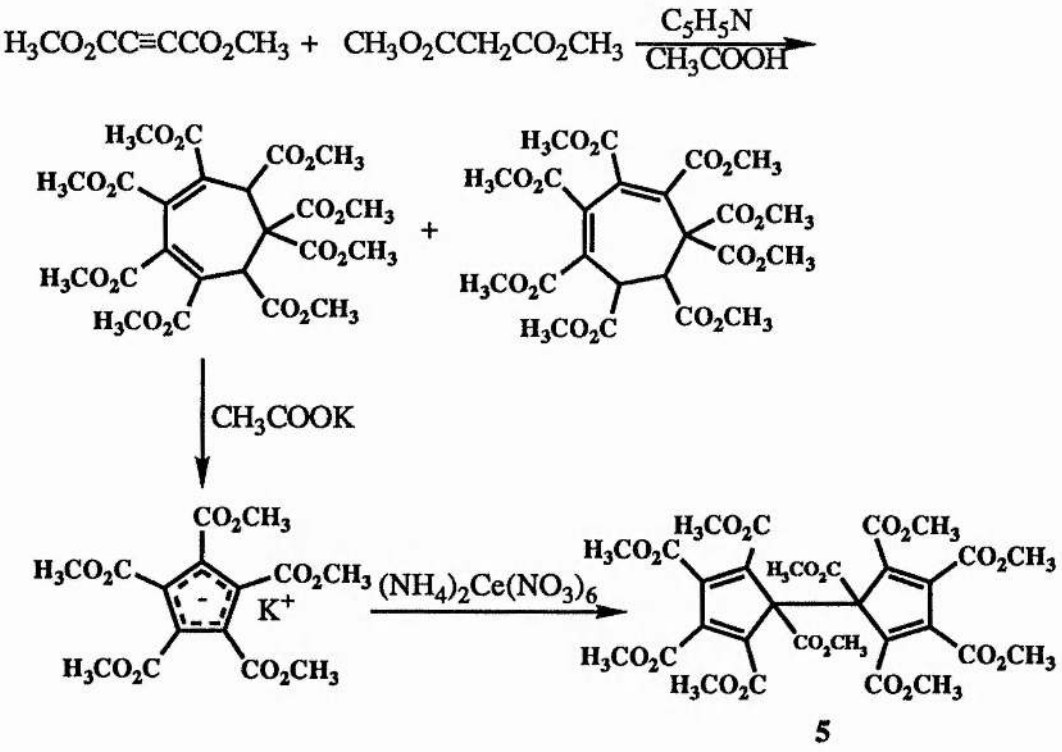
The addition of acid to the alkenol resulted in the visible elimination of water and the mass spectrum of the product gave a molecular ion of *m/z* 206. However, the compound formed was not pentaethylcyclopentadiene. ^{1}H and ^{13}C NMR spectra were too complicated to be due to a symmetrical compound and it is believed that cyclisation to give **4** was occurring. GC/MS revealed the presence of two products with almost identical retention times and with the correct molecular ion which may be due to the *cis*- and *trans*-isomers of **4**. *Exo*-cyclisation is a minor cyclisation pathway in the formation of pentamethylcyclopentadiene[40], but it appears to be a more important mode of cyclisation in the case of the pentaethyl derivative.

2.3 Decamethoxycarbonylbiscyclopentadiene.

This compound was prepared as shown below.[41,42]



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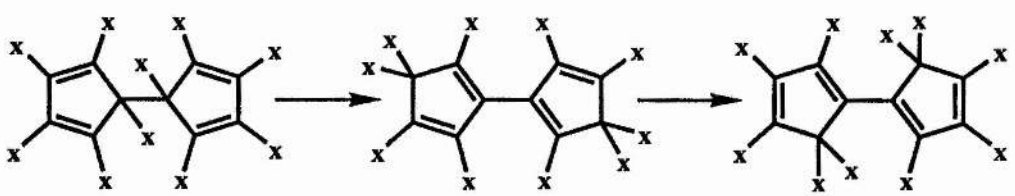
Potassium pentamethoxycarbonylcyclopentadienide was prepared by the reaction of potassium acetate with 1,1,2,3,4,5,6,7-octamethoxycarbonylcyclohepta-3,5-diene. The potassium salt was then coupled at room temperature using ceric

ammonium nitrate in aqueous methanol solution.

As photolysis of the dimer, **5**, gave the corresponding cyclopentadienyl radical,[43] we anticipated that thermolysis should also give this radical. Thermolysis of this dimer in the cavity of an ESR spectrometer at 385 K gave the corresponding pentamethoxycarbonylcyclopentadienyl radical, a(H) 0.66 G; Lit.[43] 0.61 G. However, at the same temperature as the formation of the radical occurred, a second radical formed which was a very broad, unresolved peak, which masked part of the cyclopentadienyl radical spectrum. This made determination of the stabilisation energy of the cyclopentadienyl radical impossible. It was initially assumed that contamination of the dimer was responsible for this extraneous signal, however after repeated re-crystallisation, the ^{1}H and ^{13}C showed no impurity present, yet the broad signal was still present. In order to investigate what was occurring, a solution of the dimer was heated to 120-140 °C until a red/brown colour developed and was then analysed by ^{1}H, ^{13}C NMR and mass spectrometry. It was found that the dimer had undergone a rearrangement.



5 **6**

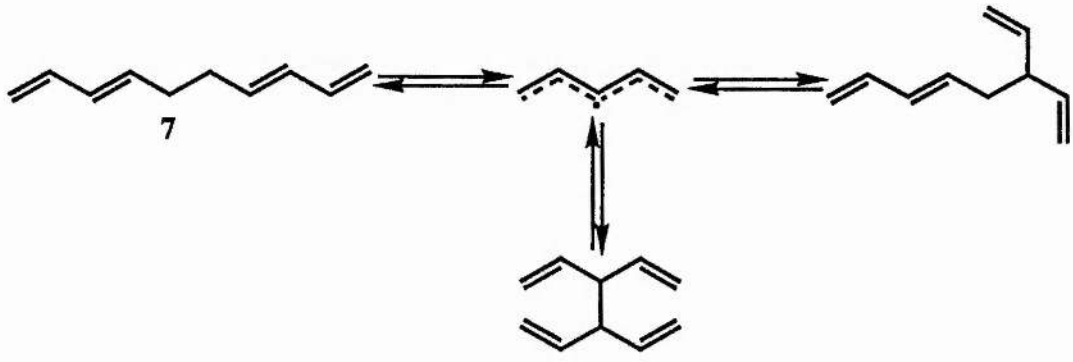
X = CO_2CH_3

What may be occurring is a 1,2-carboxyalkyl shift. It is known that H migration occurs in 9,10-dihydrofulvalene to give 1,5-dihydrofulvalene,[44,45] and that H and CH_3 substituents may migrate about a cyclopentadiene ring,[44-46] so it seems possible that a similar shift is occurring here to give the rearranged dimer, **6**. If the rearranged dimer undergoes homolytic cleavage to give a radical it would be different from the one obtained from dimer **5**. It may also be that a more facile process is loss of $COOCH_3$ to give a highly stabilised conjugated radical.

2.4 Pentadienes.

In order to determine the stabilisation energy of the pentadienyl radical, the corresponding dimer, deca-1,3,7,9-tetraene, **7**, was examined by ESR. However, product studies on the equilibrated reaction mixture showed that the dimer is not in perfect equilibrium with itself, and can re-dimerise at position C_3 as well as C_1.[47] It is possible that dimerisation at the C_3–$C_{3'}$ position may also be occurring *via* a Cope rearrangement.

Ignoring the fact that dimerisation does not always return to the initial isomer, would lead to errors in the determination of $\Delta H_f^o(R^\bullet)$ because breaking the C_5–C_6 bond in dimer **7** to give the pentadienyl radical may require a different amount of energy than breaking the C_5–C_3 or C_3–$C_{3'}$ bond in the other dimers.

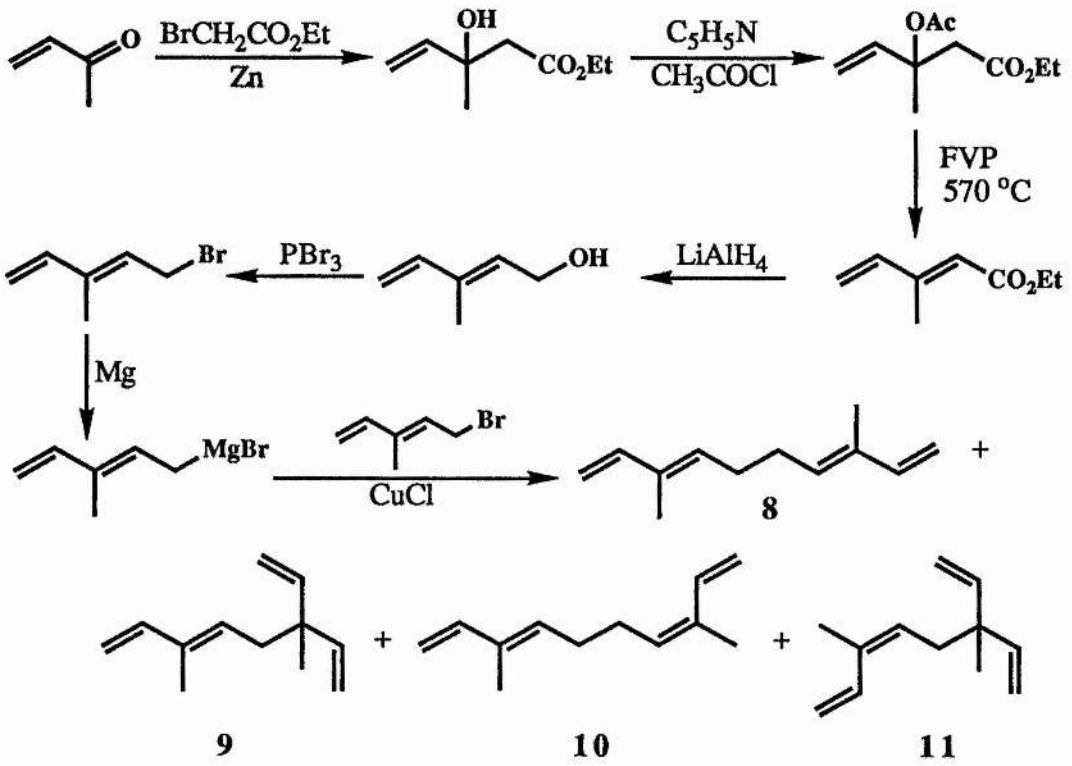


7

In order to hinder reaction at position C_3, a similar dimer, 3,8-dimethyldeca-1,3,7,9-tetraene, **8**, was prepared. The steric effect of the methyl substituent at C_3 on the corresponding 3-methylpentadienyl radical should reduce the amount of re-dimerisation occurring at this position.

The dimer was prepared according to the scheme outlined below. Reformatsky reaction of ethyl bromoacetate (using ultrasound if necessary to initiate the reaction)[48,49] with methyl vinyl ketone in the presence of activated zinc[50] gave the β-hydroxy ester, ethyl 3-methyl-3-hydroxypent-4-enoate, which was acetylated using *N*-acetyl pyridinium chloride.[51] Flash vacuum pyrolysis was used to eliminate acetic acid to give ethyl 3-methylpenta-2,4-dienoate which was then reduced to the alcohol

using lithium aluminium hydride. Bromination with phosphorus tribromide gave 5-bromo-3-methylpenta-1,3-diene.[52] Coupling of the bromide was achieved by addition of 1 mol. equivalent of bromide to 1 mol. equivalent of the corresponding Grignard reagent, in the presence of a copper (I) chloride catalyst.



Whilst the major product was the desired *trans-,trans*-3,8-dimethyldeca-1,3,7,9-tetraene, **8**, three other isomers, **9**, **10** and **11**, were also isolated and identified. It was possible to isolate dimers **8** and **9** by preparative GLC in large enough quantity for further study.

2.4.1 Thermal Rearrangement

Whilst isomer **8** was predominant in the reaction mixture, it was not the thermodynamically favoured dimer. Degassed solutions of **8** and **9** in *n*-hexadecane were heated at 200 °C and the composition was monitored by GLC (column: 10% Carbowax 20 M, 12', 100 °C).

The results obtained are given below.

Unreacted Dimer, **8**, (No heating)

This is the mixture was that obtained from preparative GLC before any heating of the sample was carried out.

t_R = GC Retention time

Dimer	t_R(mm)	Peak Height(mm)	Area(mm^2)	Relative %
11	77	1	77	0.1
9	84	11	924	1.6
10	229	32	7328	13.0[a]
8	262	184	48208	85.3

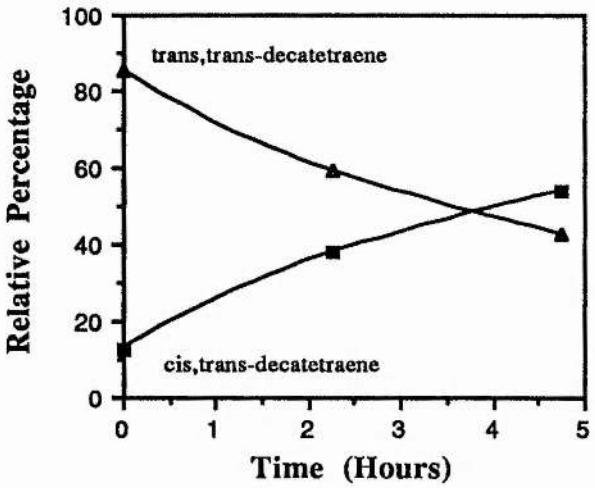
[a] Note that even though dimer **8** was separated by preparative GLC, dimer **10** has increased to 13.0% of the composition due to thermal isomerisation of isomer **8** within the oven of the chromatograph.

After 2.25 hr. at 200 °C

Dimer	t_R(mm)	Peak Height(mm)	Area(mm^2)	Relative %
11	73	4	219	0.6
9	80	10	800	1.6
10	211	63	13293	37.7
8	246	85	20910	59.4

After 4.75 hr. at 200 °C

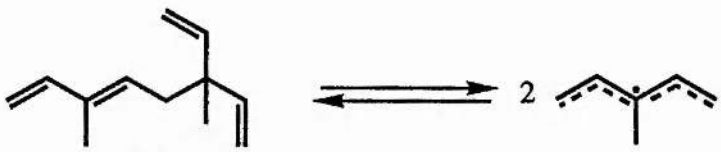
Dimer	t_R(mm)	Peak Height(mm)	Area(mm^2)	Relative %
11	71	5	355	1.4
9	79	5	395	1.6
10	206	65	13390	54.1
8	241	44	10604	42.9



It can be seen from the relative percentages of the isomers that the relative amounts of dimers **9** and **11** remain fairly constant, whilst dimer **8** decreases proportionally to the increase in dimer **10**, which suggests that dimer **8** is undergoing isomerisation to dimer **10**.

2.4.2 High Temperature ESR Study Of Pentadiene Dimers.

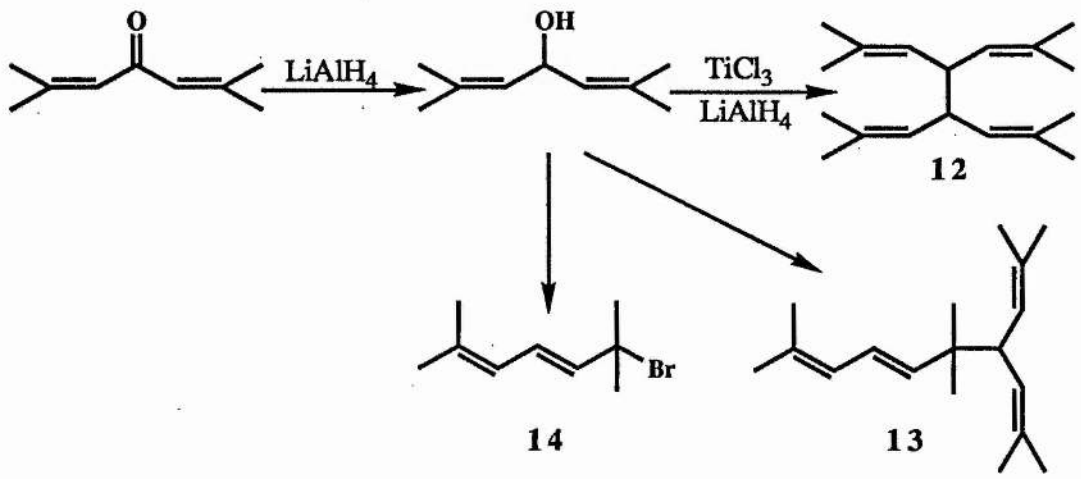
Degassed solutions of dimers **8** and **9** in *n*-hexadecane were heated in the cavity of an ESR spectrometer. Though the temperature was raised to 500 K (the maximum safe limit for the instrument), no radicals were observed for dimer **8**, but a very weak spectrum was just beginning to appear from dimer **9**.



9

As this dimer appeared to undergo homolytic cleavage more readily than dimer **8**, it may be that the dimers bonded at position C_3 are easier to cleave. It was therefore, decided to prepare a pentadiene dimer centred at C_3 (which should not dimerise at C_1) to see if it could be cleaved at a temperature in the working range of the spectrometer. It was attempted to prepare the dimer 2,7-dimethyl-4,5-bis(2-methylprop-1-enyl)octa-

2,6-diene **12**, as outlined below. 2,6-dimethylhepta-2,5-dien-4-one (phorone) was reduced to the corresponding alcohol using lithium aluminium hydride. The alcohol was then coupled using McMurrays' reagent.[53,54]



The mixture obtained unfortunately contained many isomers which proved too difficult to separate. Preparative GLC was inefficient at separation as the dimers were almost solid, however, enough of the predominant component in the mixture was isolated for analysis. It proved not to be dimer **12** but the product of C_3–C_1 dimerisation, viz. **13**. It was decided to try and prepare dimer **12** *via* coupling of the bromide in an analogous preparation to 3,8-dimethyldeca-1,3,7,9-tetraene, however, bromination gave the rearranged bromide, **14**, which proved to be very unstable. Work on this dimer was discontinued.

2.4.3 High Pressure ESR.

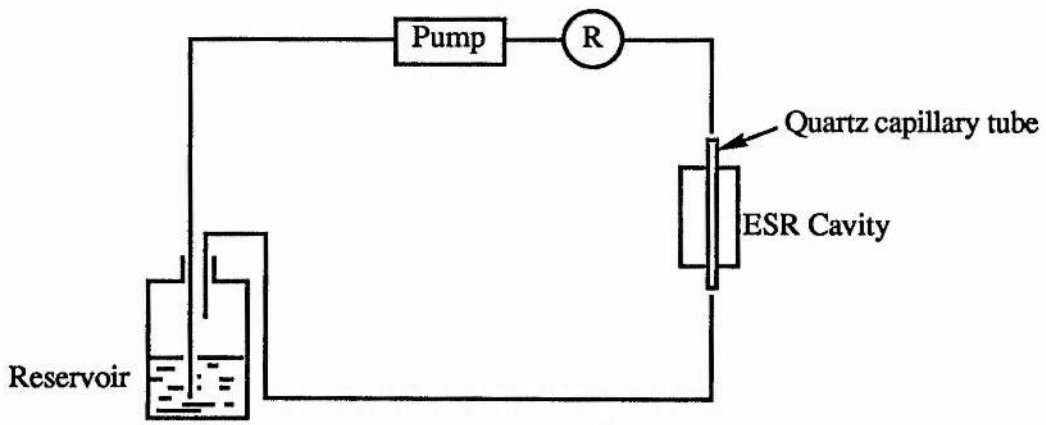
As 3,8-dimethyldeca-1,3,7,9-tetraene did not undergo homolysis to the pentadienyl radical in the accessible temperature range of the ESR spectrometer, it was decided to investigate the effect of pressure, to see whether or not high pressure would lower the temperature at which homolysis to the radical would occur.

High pressure ESR study of transient free radicals has only received limited attention. Most of the work has been carried out on inorganic transition metal

compounds, for example, crystals of chromium chalcogenide spinel, $CdCr_2Se_4$, in order to study the effect of pressure on its magnetic properties. Solid samples are normally employed and high pressure is achieved using a diamond anvil cell, operating up to 100 kbar.[55] Other work includes the use of ESR to study the effect of pressure on the chemical equilibrium of solvated electrons (up to 405 bar)[56], solvent and pressure effects on the spin exchange of nitroxide radicals in solution[57] and spectra of liposomes in a lipid bilayer (up to 3 kbar).[58]

Common to all these systems is a fixed ESR cell in which the solution remains static. This type of system is of no use for the observation of transient free radicals where a rapid build up of decomposition products would affect the observed signal. Use of a high pressure flow cell has made possible the detection of transient free radicals by ESR.[59]

A similar flow cell of the type described in the literature was built in order to study the homolysis of decatetraene to pentadienyl radicals.



R = Pressure Regulator

Azo-*iso*-butyronitrile was reported to decompose to give a well resolved spectrum of the radical in such a set up. Our system was tested using a solution of AIBN in benzene, but after a series of leaks, no signals were detected. Unfortunately, time was not available to sort out these initial teething problems and it is hoped that this work will be continued by other workers in the future.

2.5 Determination Of $\Delta H_f^o(R^\bullet)$ From Appearance Energies.

Heats of formation, ΔH_f^o, can be determined by measuring the appearance energy (AE) of particular ions, using a mass spectrometer. To define AE we can consider the ethane molecule. The first ionisation energy of ethane results from the energy change in the reaction:

$$C_2H_6 \longrightarrow C_2H_6^+ + e^-$$

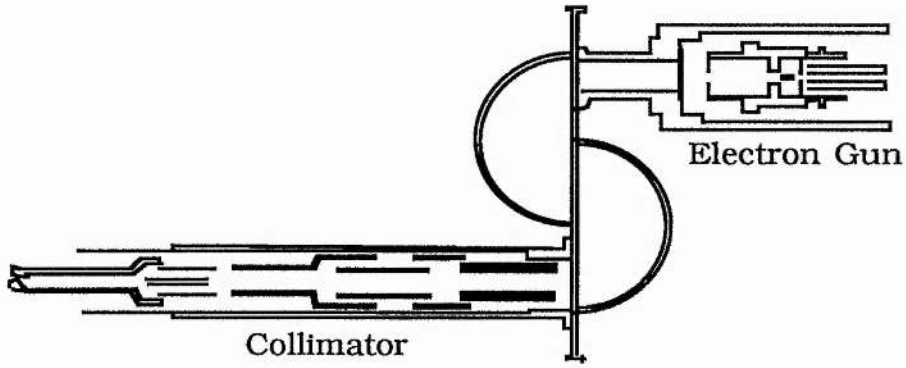
If more energy is gradually imparted in forming the $C_2H_6^+$ ion, a point will be reached at which the ion contains enough vibrational energy for it to fragment as shown:

$$C_2H_6^+ \longrightarrow CH_3^+ + CH_3^\bullet$$

The energy at which the fragment ion, CH_3^+, first appears is the appearance energy (AE) for that ion (the AE of a molecular ion is its first ionisation energy).[60] AE measurement has been used to determine $\Delta H_f^o(R^+)$ for a variety of gas phase ions[61,62], a knowledge of which is essential for full interpretation of mass spectral data[63]. AE measurements have also been used to determine $\Delta H_f^o(R^\bullet)$ for a variety of different radical types.[64-70]

In theory, the AE of a molecule can be determined using a conventional mass spectrometer, but in practice this does not give reliable results. One of the principal difficulties is that the energy spread in the bombarding electron beam, produced most conveniently by emission from a heated filament, is so large that detailed structural features in the efficiency curves for production of excited states and ions are largely obscured.

This problem has been overcome using a quadrupole mass spectrometer fitted with a two-stage double-hemispherical electron energy selector which collimates the electron beam.



Using such an electron energy selector, energy half-widths of 0.06-0.12 V in the electron beam have been obtained with operating voltages of 10-30 V in the hemispherical stages.[71]

The AE for the ionic fragmentation process;

$$AB \longrightarrow A^+ + B^\bullet + e^-$$

where the heats of formation, ΔH_f^o, of AB and $B^\bullet$ are known, is commonly used to derive ΔH_f^o values for the fragment ion A^+. In cases where A^+ is an ion whose ΔH_f^o is well established, it is equally valid to derive ΔH_f^o for the neutral fragment, the radical $B^\bullet$ and these terms are related by the equation:

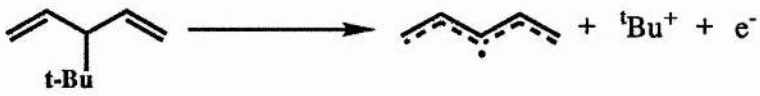
$$AE = \Delta H_{rxn} = \Delta H_f^o(A^+) + \Delta H_f^o(B^\bullet) - \Delta H_f^o(AB) \qquad (1)$$

Precursor molecules AB are preferred in which the dissociations to form the radical $B^\bullet$ are minimum energy, single bond ruptures (or molecular eliminations

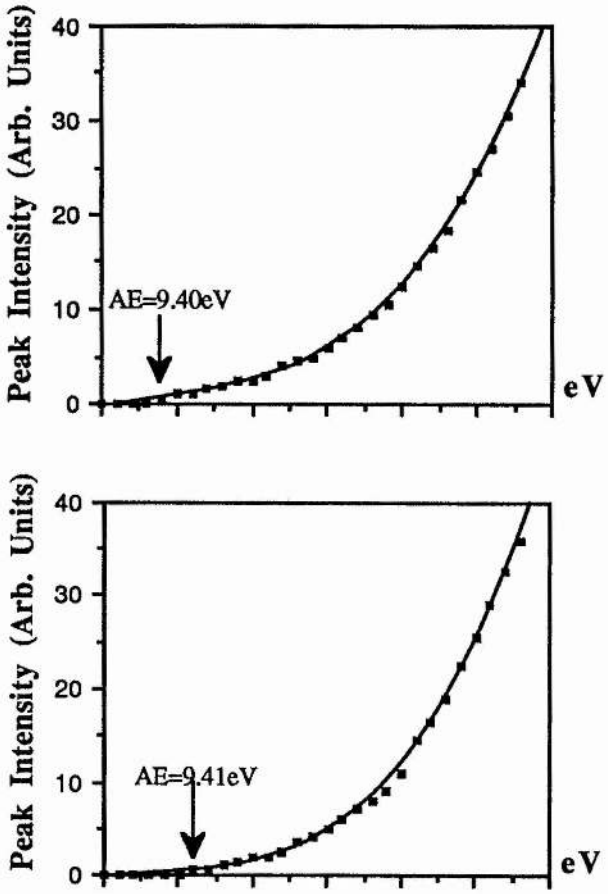
involving a six-membered transition state (*e.g.* McLafferty rearrangement)), in order to minimise uncertainties resulting from the effects of kinetic shift and reverse activation energies.[37] The neutral heats of formation must also be available, or capable of accurate estimation.[72]

In the pentadienes studied, the AEs were determined by electron impact of an energy-resolved electron beam from an electrostatic electron monochromator as described. The AE thresholds were calibrated by comparison with the threshold for H_2O^+ formation for water added to the sample stream. The measurements were carried out by Professor F.P.Lossing at Ottawa University, Canada.

We found that the dissociation of 3-*tert*-butyl-penta-1,4-diene, (3-t-BPD), was a suitable process for the measurement of $\Delta H_f^o(PD^\bullet)$, as the fragmentation products are stabilised. The main fragmentation pathway on bombardment with mono-energetic electrons gave the pentadienyl radical together with the *tert*-butyl cation which has a well established heat of formation.[73]



The AE for this process (*i.e.* appearance of *m/z* 57; $^tBu^+$) was measured as 9.41±0.01 eV, by increasing the applied electron voltage in the mass spectrometer until a signal due to the *tert*-butyl cation was observed.



The final result was obtained as the average of the above two determinations.

Now, using equation (1) we get:

$$AE = \Delta H_{rxn} = \Delta H_f^o(^tBu^+) + \Delta H_f^o(PD^\bullet) - \Delta H_f^o(3\text{-t-BPD}) \qquad (2)$$

In theory we can derive the heat of formation of 3-*tert*-butylpenta-1,4-diene from the Benson group equivalents:[23]

$$\Delta H_f^o(3\text{-t-BPD}) = 2[C_d\text{–}(H)_2] + 2[C_d\text{–}(H)(C)] + [C\text{–}(C_d)_2(C)(H)] + [C\text{–}(C)_4] + 3[C\text{–}(C)(H)_3] \qquad (3)$$

However, the group equivalent for [C–$(C_d)_2$(C)(H)] is unknown and so was estimated in the following way.

From Benson, [C–(C_d)(C)(H)] = -4.76 kcal mol^{-1} and [C–$(C_d)(C)_2$(H)] = -1.48 kcal mol^{-1}. The difference between which is +3.28 kcal mol^{-1}, that is for converting an H into a C in the presence of a C_d. Assuming the difference is the same for two C_d, from Benson [C–$(C_d)(H)_2$] = -4.29 kcal mol^{-1}, and subtracting +3.28 we get the group value = -1.0 kcal mol^{-1}.

This estimation of the [C–$(C_d)_2$(C)(H)] group equivalent was confirmed by looking at the dissociation of 3-*iso*-propylpenta-1,4-diene, (3-i-PPD). For this compound, the major dissociation pathway is not the formation of the *iso*-propyl cation and the pentadienyl radical, but a fragmentation into the penta-1,3-dienyl cation (note the isomerisation) and propylene.

Since the formation of the *iso*-propyl cation was not the major fragmentation the AE for the appearance of the *iso*-propyl cation (*m/z* 43) is untrustworthy for determining $\Delta H_f^o(PD^\bullet)$. However, the AE for the pentadienyl cation (*m/z* 68) determined to be 9.28 eV by the method described above is useful for measuring ΔH_f^o(3-i-PPD).

Again, using equation (1) we find:

$$AE = \Delta H_f^o(PD^+) + \Delta H_f^o(\text{propylene}) - \Delta H_f^o(\text{3-i-PPD}) \qquad (4)$$

Converting eV to kcal mol^{-1}; 9.28 eV = 9.28/4.34 x 10^{-2} = 214 kcal mol^{-1}.

Substituting the values into equation (4) we get;

$(214) = (216) + (4.88) - \Delta H_f^o(3\text{-i-PPD})$

$\Delta H_f^o(3\text{-i-PPD}) = 6.88$ kcal mol^{-1}.

If we derive ΔH_f^o(3-i-PPD) from the Benson group equivalents;

$$\Delta H_f^o(3\text{-i-PPD}) = 2[C_d\text{–}(H)_2] + 2[C_d\text{–}(H)(C)] + [C\text{–}(C_d)_2(C)(H)] + [C\text{–}(C)_3(H)] + 2[C\text{–}(C)(H)_3]$$
$$= 6.9 \text{ kcal mol}^{-1}.$$

which is in perfect agreement with the experimentally derived value of ΔH_f^o(3-i-PPD) which shows that our derived group value of $[C\text{–}(C_d)_2(C)(H)]$ is very good.
Now we can derive ΔH_f^o(3-t-BPD), by using the calculated group value for $[C\text{–}(C_d)_2(C)(H)]$ in equation (3);

$$\Delta H_f^o(3\text{-t-BPD}) = 2(6.26) + 2(8.59) + (-1.0) + (0.50) + 3(-10.20)$$
$$= -1.4 \text{ kcal mol}^{-1}.$$

Now the AE for the *tert*-butyl cation from 3-t-BPD was measured to be 9.41 eV which is $9.41/4.34 \times 10^{-2} = 217$ kcal mol^{-1}
Then substituting into equation (2) we get;

$(217) = (166) + \Delta H_f^o(PD^{\bullet}) - (-1.4)$
So, $\Delta H_f^o(PD^{\bullet}) = 49.6$ kcal mol^{-1}.

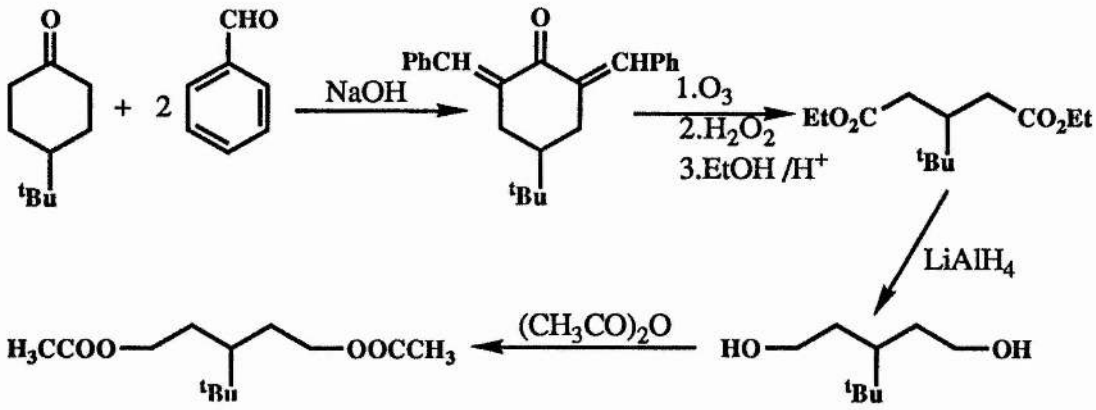
This is in excellent agreement with the value of 50±3 kcal mol^{-1} quoted in McMillan and Goldens 1982 review[74], (see § 2.9).

2.6 3-Substituted Penta-1,4-dienes.

2.6.1 3-*tert*-Butylpenta-1,4-diene.

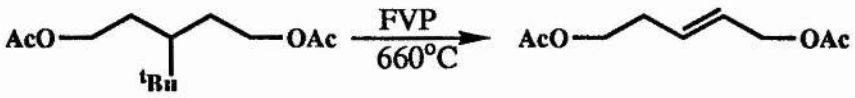
As a considerable amount of material was required for the photoacoustic calorimetry measurements, it was decided to devise a large scale preparative route to 3-*tert*-butylpenta-1,4-diene (3-t-BPD). The only literature reference to 3-t-BPD is that of Yasuda *et al.*[75] who observed 3-t-BPD in the reaction mixture of pentadienyl potassium and *tert*-butyl bromide. It is not clear whether this method was used for preparative work, but repeated attempts in these laboratories proved unsuccessful at preparing 3-t-BPD by this method. The compound was not even detected in the mixture by GC/MS. A more suitable synthesis was therefore required.

It is known that pentane-1,5-diol diacetate under pyrolysis conditions can eliminate acetic acid to give penta-1,4-diene and it was decided to try an analogous route using 3-*tert*-butylpentane-1,5-diol diacetate. This was prepared according to the scheme outlined below:



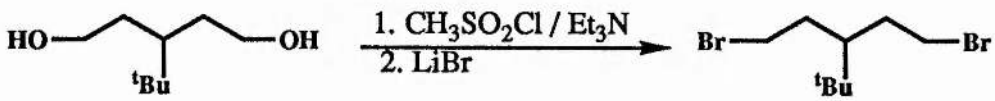
The dibenzylidene derivative of 4-*tert*-butylcyclohexanone was prepared using benzaldehyde in the presence of base. Ozonolysis of the derivative, followed by oxidation with hydrogen peroxide gave a mixture of 3-*tert*-butylpentane-1,5-dioic acid and benzoic acid. Separation was achieved by esterification and distillation of the esters.[76] The diester was reduced to the diol using lithium aluminium hydride and the diol was then converted to the diacetate using acetic anhydride. Unfortunately, flash

vacuum pyrolysis failed to produce 3-t-BPD. It appears that the preferential loss is the *tert*-butyl group before acetic acid elimination occurs.



Elimination of water from the diol using phosphoric acid also proved unsuccessful. The ditosylate compound was prepared from the diol[77] and attempts were made to form the diene from this. Two methods of alkene formation by elimination of *p*-toluenesulphonic acid have been reported, but in both cases only secondary or tertiary tosylates had been used. Heating the ditosylate in DMSO[78] up to 170 °C was tried but no diene was formed. A second method involves heating a tosylate with tetra-*n*-butylammonium oxalate.[79]. Unfortunately the literature reference did not give an experimental procedure and did not mention in what state the oxalate should be (*e.g.* anhydrous or hydrated). Preparation of the oxalate from tetra-*n*-butylammonium hydroxide and oxalic acid gave a solution of the oxalate but even after evaporation a liquid still remained. One of the fascinating properties of this compound is that it exists as a clathrate compound within a cage of water molecules, and in fact it has been reported to possess 58 waters of hydration! Not surprisingly, even drying at 130 °C/ 1 mmHg proved unsuccessful, a slurry still remained. However, attempted reaction of the ditosylate with the slurry was carried out but again no reaction occurred.

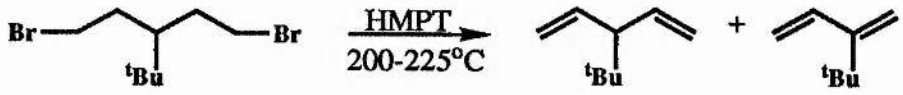
It was decided to try and eliminate HBr from the corresponding dibromide which was prepared from the diol *via* the mesylate.



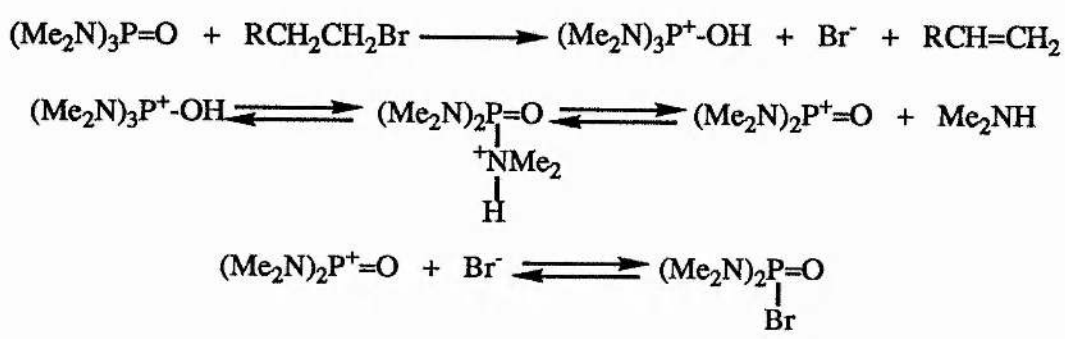
F.V.P. again proved useless as the *tert*-butyl group was lost before dehydrobromination occurred. If this method had led to elimination of HBr it still may not have formed the desired product because under pyrolysis conditions the diene

which formed may undergo a rearrangement. It has been reported that pyrolysis of pentadienes may give rise to cyclopentadienes.[80]

Distillation in DBU[81,82] or neat quinoline[83] also proved fruitless. However, distillation in HMPT[84] at *ca.* 200-225 °C did give 3-t-BPD.



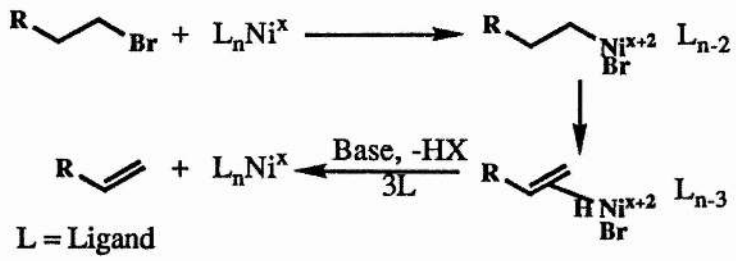
Elimination occurs *via* the following mechanism:[85]



Note, that the conditions required to achieve this reaction were so harsh that a certain amount of *tert*-butylbuta-1,3-diene was also identified in the mixture. Unfortunately, one of the problems of using such high temperatures was that a lot of the product polymerised. Maximum yield was therefore best obtained when blowing a stream of nitrogen gas through the reaction mixture whilst set up in a distillation apparatus and trapping the distillate in a cardice/acetone cooled trap. The diene came over readily, contaminated with amine and was purified by preparative GLC.

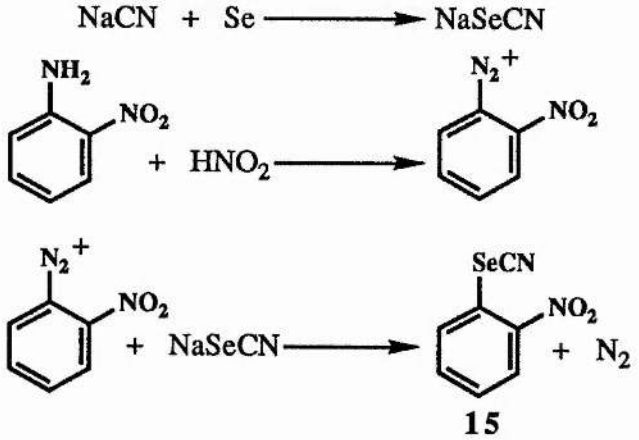
Whilst this route did give the diene, it was not satisfactory on a large scale, and so two further methods were attempted in order to try and increase the yield.

The bromide can be dehydrobrominated quite well at room temperature using a very mild elimination method which involved the use of dichloronickel (II) tris(triphenylphosphine), *n*-butyl lithium and DBU.[86,87] The reaction works by first forming an intermediate nickel complex.



Unfortunately, the amount of reagent required to eliminate HBr from both ends of the molecule made it very difficult to recover the diene and hence it was impractical to use, however it appears to be a very good method of dehydrobromination in cases where the alkene obtained is not so volatile and is easier to recover.

It is known that selenoxides are unstable at room temperature and that terminal selenoxides decompose to give terminal alkenes. The selenium reagent used in this reaction is *o*-nitrophenylselenocyanate, **15**, which was prepared as shown;[88,89]



15

The selenocyanate was then reacted with the diol in the presence of tri-*n*-butylphosphine to give the diselenide[90]

$$ArSeCN + Bu_3P \longrightarrow ArSeP^+Bu_3CN^-$$

$$ArSeP^+Bu_3CN^- + RCH_2OH \longrightarrow RCH_2OP^+Bu_3 + HCN + ArSe^-$$

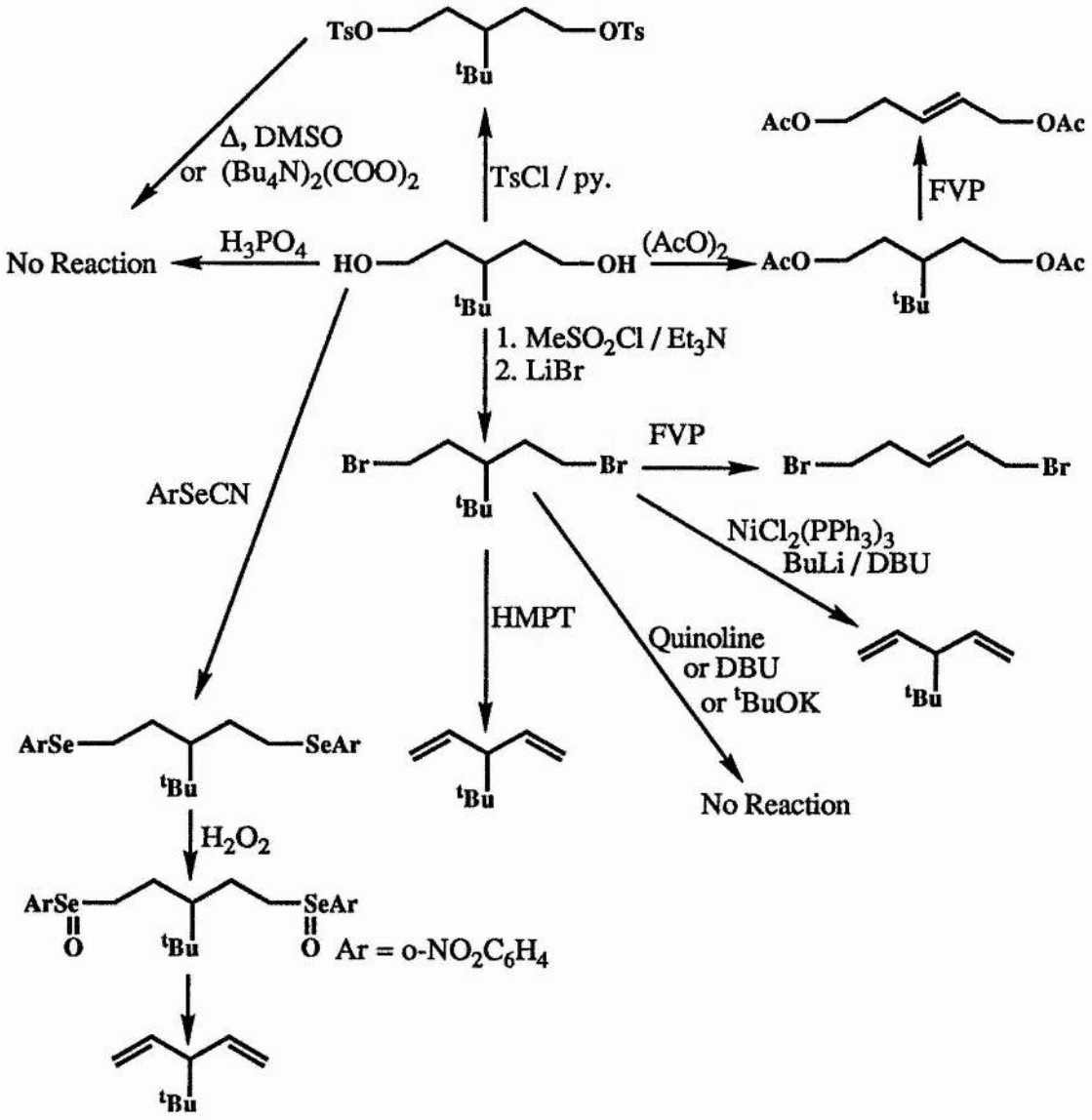
$$RCH_2CH_2OP^+Bu_3 + ArSe^- \longrightarrow RCH_2SeAr + Bu_3P{=}O$$

which was then oxidised to the diselenoxide using hydrogen peroxide.[88] This method

worked, but a similar problem to the nickel chloride route made it inefficient. The organoselenium residue from the reaction was in such large amount that multiple purification steps by column chromatography were required. As the diene was highly volatile most of it was probably lost in this work up, however enough was obtained to identify it conclusively.

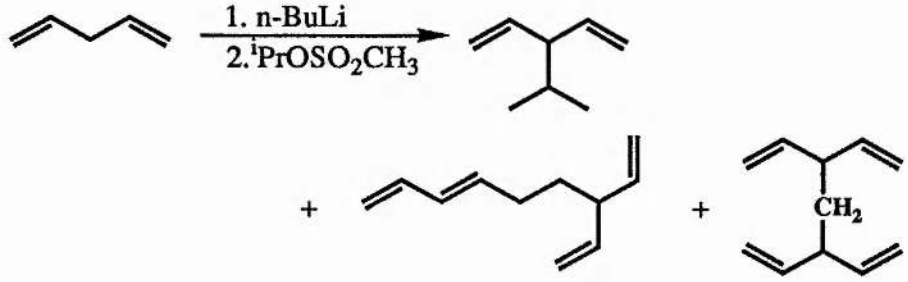
Whilst the HMPT route had several drawbacks it was the chosen route to prepare the diene.

Overall, the routes attempted to prepare 3-t-BPD can be summarised as;



2.6.2 3-*iso*-Propylpenta-1,4-diene.

Fortunately, in preparing 3-*iso*-propylpenta-1,4-diene, a short cut was found which enabled the long preparative route described above to be avoided. The reaction of *iso*-propyl *p*-toluenesulphonate with potassium pentadienide has been shown to give 3-*iso*-propylpenta-1,4-diene. As a great many methanesulphonate esters have been prepared in this work (Chapter Four), it was decided to see if the reaction could be carried out with *iso*-propyl methanesulphonate. Lithium pentadienide was prepared by the addition of *n*-butyl lithium to penta-1,4-diene. The pentadienide was then added to a solution of *iso*-propyl methanesulphonate under nitrogen.



16 **17**

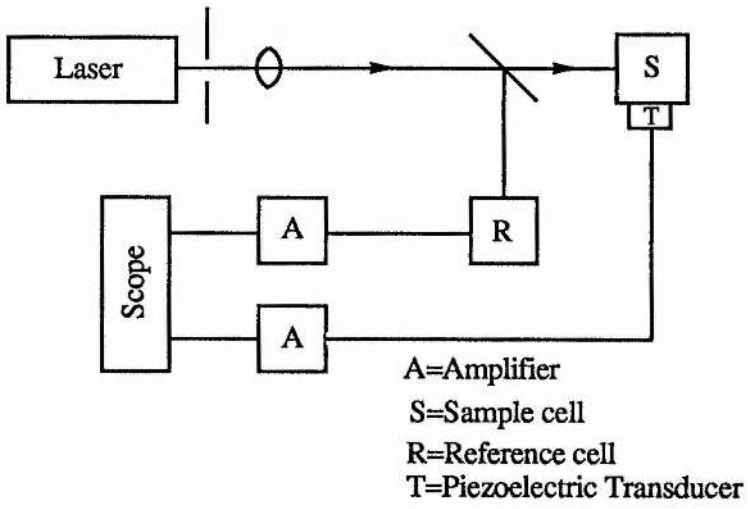
Apart from the formation of 3-*iso*-propylpenta-1,4-diene, several other components were identified in the mixture. Methanesulphinic acid was extracted from the residue. The most surprising find was the $C_{11}H_{16}$ tetraenes, **16** and **17**. It would be expected to observe coupling of the pentadienide to give $C_{10}H_{14}$ dimers, yet the pentadienes were in fact coupled through a methylene unit.

Whilst neither the 3-*tert*-butyl- nor 3-*iso*-propylpenta-1,4-diene was obtained in large enough quantity for the photoacoustic experiments, enough material was available for the appearance energy experiments previously described.

2.7 Photoacoustic Calorimetry.

The technique of pulsed laser photoacoustic calorimetry was first used in 1983 to determine the heat of formation of a non-emitting metastable photochemical intermediate, the radical pair formed in the photoreduction of triplet benzophenone by aniline.[91] The technique was later applied to the determination of the heat of reaction of carbenes[92] and to determine metal carbonyl bond strengths.[93] It was not until 1985, that Griller *et al.* used the technique for the determination of the heat of formation of free radicals.[94]

The photoacoustic approach to thermochemistry is very simple. It does not rely upon any theory and all of its features can be tested experimentally. A picture (overleaf) and a block diagram of the photoacoustic apparatus is shown.[95]



Pulses from a nitrogen laser (λ=337.1 nm; pulse width 10 ns) were used as the irradiation source. The light first passed through an iris where most of the laser energy was discarded. To ensure that only a fine beam passed through the centre of the sample cell, a low powered lens was used to correct for the slight divergence of the beam. The light then passed through the sample chamber which was a normal UV flow cell which contained a solution of the photolabile substrate. Photolabile molecules in the beam absorbed quanta of light and some of this energy was used in the photochemical

reaction; any excess was released as heat into the solution where it caused a shockwave which was transmitted through the solution at the speed of sound to the cell wall. Here, the primary wave and its many reflections were detected by a high frequency piezoelectric transducer and recorded on a storage oscilloscope.

When heat liberation was rapid with respect to the microphone response, the amplitude of the first wave to reach the transducer was proportional to the amount of heat liberated. Thus, the system functions as a simple calorimeter. Calibration was achieved by use of a reference cell which consisted of a second photoacoustic arrangement of a cuvette and a transducer. The reference cell was filled with an optically dilute solution of *o*-hydroxybenzophenone in *iso*-octane. *o*-Hydroxy-benzophenones are ideally suited for reference purposes as they convert all of the absorbed light energy into heat in a few picoseconds. On prolonged irradiation of the reference cell, some drift occurs due to small convection currents being set up in solution. However, this can easily be overcome by flowing the solution through the cell with a peristaltic pump. The sample cell itself can be operated in a continuous flow mode if the build up of by-products is a problem, though this is not normally employed as it requires a lot of sample.

The most commonly used photolabile substrate is di-*tert*-butyl peroxide which dissociates to give two *tert*-butoxyl radicals. Therefore, to a good approximation, the heat released into the solution, ΔH_{obs}, will be equal to the difference between the photon energy and the heat of reaction, ΔH_R, which is given by the O–O bond dissociation energy of the peroxide. However, in solution the viscosity of the medium will cause a proportion of the initially formed *tert*-butoxyl radical pairs to recombine before they escape the solvent cage and diffuse as free radicals into the bulk solution. The photoacoustic arrangement can be used to measure the quantum yield, Φ, or cage effects for the photolysis, and ΔH_{obs} is related to Φ by the equation;

$$\Delta H_{obs} = 84.8 - \Delta H_R \Phi \qquad (1)$$

A plot of normalised photoacoustic response, N, *versus* light absorbed by the sample, (1–T), gives a linear plot, with slopes a_R and a_S for reactant and standard respectively and it has been shown that, as the standard converts all light absorbed into heat energy;

$$\Delta H_{obs} = 84.8(a_R/a_S) \quad (2)$$

Substituting into equation (1) gives;

$$\Delta H_R = (84.8/\Phi)(1 - a_R/a_S) \quad (3)$$

The nature of the substrate, RH, must be such that the rate of reaction (ii) is rapid compared to transducer response and the experimental conditions are such that the radical product R$^\bullet$ is long lived on this timescale.

$$^tBuOOBu^t \longrightarrow 2\,^tBuO^\bullet \qquad (i)$$

$$^tBuO^\bullet + RH \longrightarrow {}^tBuOH + R^\bullet \qquad (ii)$$

The heat evolved in the above reactions, ΔH_R, therefore represents the combined thermochemistry for these reactions and hence;

$$\Delta H_R = 2\Delta H_f^o(^tBuOH) + 2\Delta H_f^o(R^\bullet) - \Delta H_f^o(^tBuOOBu^t) - 2\Delta H_f^o(RH)$$

Using ΔH_f^o for ^tBuOH, $^tBuOOBu^t$ and H$^\bullet$ and the quantum yield for photolysis of peroxide, Φ, gives;

$$BDE(R–H) = \Delta H_f^o(R^\bullet) + \Delta H_f^o(H^\bullet) - \Delta H_f^o(RH)$$

$$BDE(R–H) = \Delta H_R/2 + 85.1$$

Three different penta-1,4-dienes were studied, 3-hydroxypenta-1,4-diene, 3-methylpenta-1,4-diene and penta-1,4-diene itself. In each case solutions of the dienes in benzene were degassed using argon (several freeze-pump-thaw cycles for penta-1,4-diene). Spectroscopically pure benzene was used as a solvent because it has good photoacoustic properties. At each photoacoustic measurement, the absorbance was recorded at 337 nm (laser wavelength) to ensure that the reactant was not absorbing, or more important that no impurities or by-products formed were absorbing. The absorbance at 550 nm was also recorded to act as an absorbance check over a wide range.

The ratio of amplitudes of the sample and reference peaks were recorded on a storage oscilloscope. The amplitude of the reference cell was not found to alter during each run.

In the case of dilute solutions, the spectrometer can be calibrated using neat solvent, however, as in the case of the pentadienes, high concentration (3-5 M) required calibration on the pentadiene solution itself, as the large quantity of reactant in solution would appreciably alter the photoacoustic response of the solution. Calibration was carried out by the addition of a known quantity of *o*-hydroxybenzophenone to the reactant solution. The ratio of sample signal/reference signal was recorded for 4-5 readings over *ca.* 5-10 minutes, after which the cell was washed thoroughly with spectroscopically pure benzene. Another portion of *o*-hydroxybenzophenone was added and the process repeated.

Also monitored during each run is the time (t in μs) between the laser pulse and the photoacoustic signal being detected. This should not change appreciably from the start to finish of the experiment or it indicates that there has been a change in the photoacoustic properties of the solution. t is very much dependent on the position where the laser strikes the sample cell and its height above the transducer, and therefore this needs to be optimised to obtain a sharp symmetrical peak with little noise. During calibration t does not normally alter as *o*-hydroxybenzophenone converts all the absorbed light energy into heat in a few picoseconds, however, a slight alteration in t is

usually observed in the peroxide induced experiment as the addition of peroxide slightly alters the photoacoustic properties of the solvent.

The time difference (Δt in μs) between the maximum and minimum of the signal was also monitored and should not change during the experiment.

The amount of calibrant added was such that throughout the entire experiment the range of the optical density (absorbance) did not exceed *ca.* 0.15. Once calibration was complete we have for a particular solution containing from zero, steadily increasing amounts of *o*-hydroxybenzophenone, with 4-5 photoacoustic readings at each concentration. At each point the sample/reference points were averaged and the ratio calculated (*i.e.* the ratio is the normalised amplitude).

A plot of N *versus* (1 – T) gave a straight line (N = normalised amplitude;

1 – T = optical density, when A is small $A \sim (1 - T) = (1 - 10^{-A})$).

Once calibration was complete, the entire experiment was repeated using di-*tert*-butyl peroxide in place of *o*-hydroxybenzophenone.

From the plot of N *versus* (1 – T) for both calibration and reaction we get;

slope; reactant/di-*tert*-butyl peroxide $= a_R$

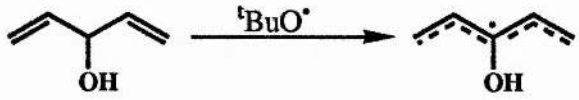
slope; reactant/hydroxybenzophenone $= a_S$

Φ, the efficiency of hydrogen abstraction was assumed to be *ca.* 0.85

An accurate knowledge of the rates of hydrogen abstraction from the penta-1,4-dienes by *tert*-butoxyl radicals is important. The rate constants, k_R, for the 3-hydroxy-, 3-methyl- and parent penta-1,4-diene are shown in Table 1. The rate constants represent the overall reactivity of the dienes towards *tert*-butoxyl radicals. *tert*-Butoxyl radicals tend to abstract rather than add where allylic systems are concerned. The fact that the rate of hydrogen abstraction from penta-1,4-diene is faster than that of the 3-hydroxy analogue is surprising considering the stabilising ability of oxygen adjacent to a radical site. The fact that k_R decreases along the series R = H, OH, CH_3 is probably due to increasing steric hindrance.

2.7.1 Penta-1,4-dien-3-ol.

Previous work carried out at concentrations of 0.5 and 1.0 mol dm^{-3} proved unsatisfactory as the results varied with each run and the values obtained were too high. This is because the abstraction reaction was relatively slow.



Thus, a 3.0 mol dm^{-3} solution was used; a high concentration ensures that a higher concentration of radicals is obtained.

The results were;

Amount of Calibrant (cm^3)	Photoacoustic Response Sample	Reference	Absorbance	1–T	N	Corrected 1–T
0.0	9.2	41.5	0.01420	0.0322	0.221	0.000
0.3	26.2	42.5	0.05600	0.1210	0.626	2.853
0.2	40.3	42.8	0.08990	0.1870	0.942	4.973
0.13	51.5	43.0	0.11870	0.2391	1.189	6.648
0.09	67.6	43.6	0.16600	0.3177	1.550	9.170

a_S (after linear regression) = 4.68

Amount of Peroxide (cm^3)	Photoacoustic Response Sample	Reference	Absorbance	1–T	N	Corrected 1–T
0.0	9.2	42.1	0.01600	0.0362	0.219	0.000
0.8	28.4	42.6	0.04940	0.1075	0.667	2.046
0.6	45.3	43.2	0.08000	0.1682	1.049	3.788
0.5	61.9	43.7	0.11250	0.2282	1.416	5.508
0.43	81.2	44.0	0.15440	0.2992	1.845	7.544

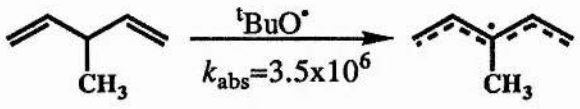
a_R (after linear regression) = 6.19

If Φ is taken to be 0.85 the BDE (C–H) = 69.0±0.6 kcal mol^{-1}.

If Φ is taken to be 0.82 the BDE (C–H) = 68.4±0.6 kcal mol^{-1}, which shows that any uncertainty in Φ does not have too large an effect on the value of the bond dissociation energy.

2.7.2 3-Methylpenta-1,4-diene.

The reaction of *tert*-butoxyl radicals with 3-methylpenta-1,4-diene was expected to be slower than for the 3-hydroxy analogue. The precise rate of hydrogen abstraction was measured by laser flash photolysis.



Like the 3-hydroxy compound, the 3-methylpenta-1,4-diene had been examined previously at concentrations of 0.5 and 1.0 mol dm^{-3} with varying results and hence a 3.0 mol dm^{-3} solution was now used.

The results were;

Amount of Calibrant (cm^3)	Photoacoustic Response Sample	Reference	Absorbance	1–T	N	Corrected 1–T
0.0	7.4	43.2	0.00007	0.0002	0.170	0.000
0.3	28.2	44.0	0.04200	0.0922	0.653	571.039
0.22	46.4	44.0	0.07960	0.1675	1.055	1038.268
0.15	59.5	43.8	0.10980	0.2234	1.358	1385.326
0.14	78.4	44.6	0.15620	0.3021	1.758	1873.676

a_S (after linear regression) = 5.28

Amount of Peroxide (cm^3)	Photoacoustic Response Sample	Reference	Absorbance	1–T	N	Corrected 1–T
0.0	6.7	42.7	0.00030	0.0007	0.157	0.000
0.8	27.7	43.6	0.03510	0.0776	0.635	111.513
0.7	48.4	44.0	0.07210	0.1530	1.100	220.672
0.55	67.2	44.5	0.11010	0.2239	1.510	323.510
0.5	90.7	44.6	0.16090	0.3096	2.036	447.658

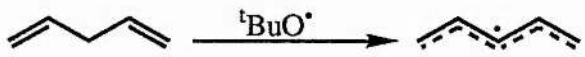
a_R (after linear regression) = 6.06

BDE (C–H) = 77 kcal mol^{-1}

The bond dissociation energy of the 3-methyl compound is higher than that of the 3-hydroxy analogue as the hydroxy substituent makes the C–H bond weaker. Since this result was obtained in the summer of 1989, it has since been repeated with a 5.5 mol dm^{-3} solution and virtually the same results were obtained. The value for the C–H bond dissociation energy can now be taken to be 76.6±0.6 kcal mol^{-1}.

2.7.3 Penta-1,4-diene.

Owing to the limited amount of sample available, the experiment was carried out in a slightly different manner. Neutral density filters were employed to regulate the laser intensity. Whilst the technique is easier than the other procedure, it is not normally used because the S/N ratio is decreased and the signals become small and noisy. The same sample remains in the cell throughout the experiment.



The experiment was carried out at three different concentrations, 3.0, 4.1 and 5.0 mol dm^{-3} in benzene.

The results obtained were;

Penta-1,4-diene, 3.0 mol dm^{-3} in benzene, including 0.25 cm^3 *o*-hydroxybenzophenone.

Neutral Density Filter	Photoacoustic Response	
	Sample	Reference
100	40.4	62.3
63	25.1	39.2
45.5	14.3	22.5
30	11.3	17.3
16	6.7	10.3

a_S (after linear regression) = 1.62

Penta-1,4-diene, 3.0 mol dm^{-3} in benzene, including 1.25 cm^3 di-*tert*-butyl peroxide.

Neutral Density Filter	Photoacoustic Response	
	Sample	Reference
100	41.0	75.3
63	24.5	44.3
45.5	14.6	26.6
30	12.2	22.0
16	6.8	12.4

a_R (after linear regression) = 1.75

BDE (C–H) = 81 kcal mol^{-1}.

Penta-1,4-diene, 4.1 mol dm^{-3} in benzene, including 0.25 cm^3 *o*-hydroxy-benzophenone.

Neutral Density Filter	Photoacoustic Response	
	Sample	Reference
100	40.2	65.6
63	24.8	41.2
48.5	18.8	31.0
45.5	14.2	23.6
37	13.8	23.2
30	12.2	20.0
16	6.3	10.6

a_S (after linear regression) = 1.63

Penta-1,4-diene, 4.1 mol dm^{-3} in benzene, including 1.25 cm^3 di-*tert*-butyl peroxide.

Neutral Density Filter	Photoacoustic Response	
	Sample	Reference
100	40.2	84.4
63	22.6	49.6
48.5	19.4	41.2
37	14.8	31.2
30	12.0	25.2
16	6.6	13.8

a_R (after linear regression) = 1.85 (corrected for a change in optical density)

BDE (C–H) = 78.3 kcal mol^{-1}

Penta-1,4-diene, 5.0 mol dm^{-3} in benzene, including 0.25 cm^3 *o*-hydroxybenzophenone.

Neutral Density Filter	Photoacoustic Response	
	Sample	Reference
100	40.3	65.2
63	24.3	39.3
48.5	19.5	31.6
37	14.4	23.6
30	12.3	19.9
16	6.4	10.4

a_S (after linear regression) = 1.63

Penta-1,4-diene, 5.0 mol dm^{-3} in benzene, including 1.25 cm^3 di-*tert*-butyl peroxide.

Neutral Density Filter	Photoacoustic Response	
	Sample	Reference
100	40.7	76.5
63	24.7	47.2
48.5	20.0	38.0
37	14.1	26.9
30	12.0	22.4
16	6.7	12.4

a_R (after linear regression) = 1.89

BDE (C–H) = 76.4 kcal mol^{-1}

The result obtained with the highest molar concentration of penta-1,4-diene was taken to be the optimum result. The result obtained for penta-1,4-diene is in good agreement with the literature value for the bond dissociation energy (77±3 kcal mol^{-1}). Not surprisingly, the value of the 3-methyl derivative is practically identical to the parent derivative. The bond dissociation energy for the 3-hydroxy derivative is reduced to 69 kcal mol^{-1} by the presence of the hydroxy group at C_3.

Overall the results were;

Table 1

R	k_R x 10^6 $M^{-1}.s^{-1}$	BDE (C–H) kcal mol^{-1}
H	4.5±0.8	76.4±0.6
CH_3	3.5±0.1	76.6±0.6
OH	15.0±1.0	69.0±0.6

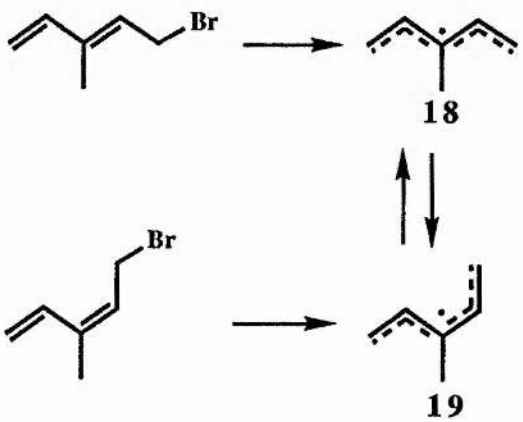
2.8 Energy Barriers To Rotation.

The stabilisation energy of the pentadienyl radical is related to the barrier of rotation about the C_2–C_3 bond, E_i, by the equation;

$$E_i = V_2 + SE(PD^{\bullet}) - SE(allyl)$$

where V_2 is the small but experimentally inaccessible barrier to rotation about the C_2–C_3 single bond in the absence of delocalisation and SE(allyl) is the stablisation energy of the allyl radical. In favourable cases, the rotation barriers in delocalised radicals can be determined by the ESR exchange method. This method has been used to determine the energy barrier to rotation for the pentadienyl radical, which was generated in the cavity of an ESR spectrometer by bromine abstraction from 5-bromopenta-1,3-diene using trimethyltin radicals.[29]

We investigated the use of this technique in an attempt to observe the exchange broadening and hence derive the stabilisation energy of several 3-substituted pentadienes. The 3-methylpentadienyl radical, (Figure 2), was generated by bromine abstraction from 5-bromo-3-methylpenta-1,3-diene using photochemically generated trimethyltin radicals, and spectra were observed in the range 290-450 K.



Unfortunately, the *cis*- and *trans*-bromides proved to be inseparable by preparative GLC and so were examined as a mixture. The major conformer, **18**, was

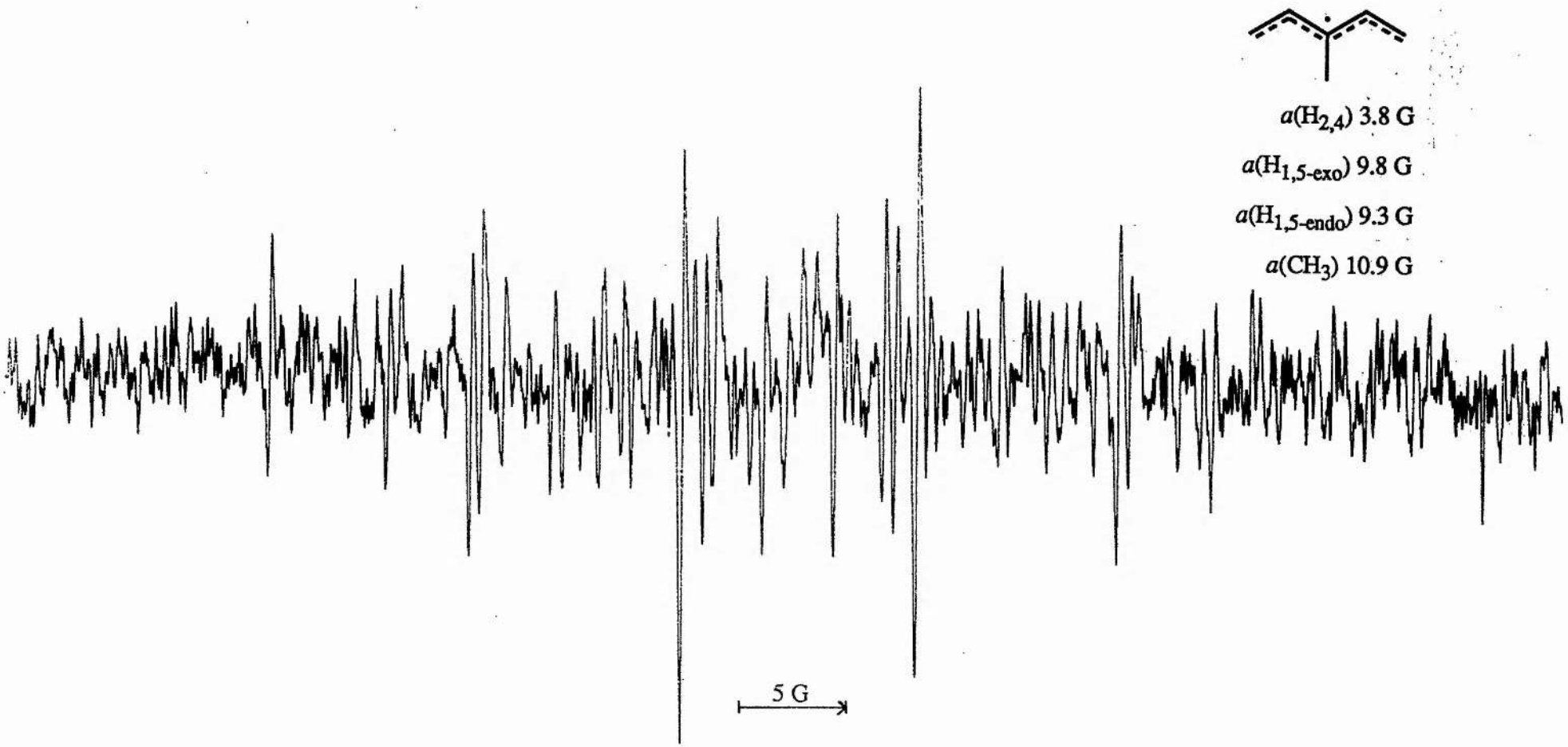
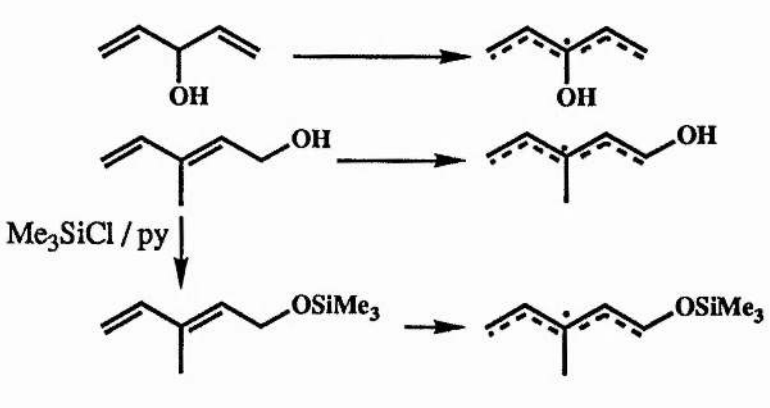


Figure 2. ESR Spectrum Of The 3-Methylpentadienyl Radical.

readily observed at 289 K with hyperfine splittings the same as reported in the literature.[13]

The minor conformer, **19**, though visible was too weak for definitive analysis. As the temperature was increased, exchange broadening was observed, with coalescence at *ca.* 330 K. Because the proportion of the minor isomer and its hyperfine splittings could not be determined, the exchange broadening could not be matched to computer simulated spectra. However, it is likely that the hyperfine splittings of the minor conformer are virtually the same as those of the analogous parent pentadienyl radical. Because the coalescence temperature is the same, then the barrier to rotation about the C_2–C_3 bond in the 3-methylpentadienyl radical must be virtually the same as that of the pentadienyl radical and hence $SE^{ESR} = 25$ kcal mol^{-1}.

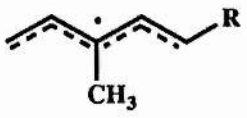
The 3-hydroxypentadienyl, 1-hydroxy-3-methylpentadienyl and 1-trimethylsilyloxy-3-methylpentadienyl radicals were generated by hydrogen abstraction from the corresponding dienes to give good ESR spectra.



In each case however, only the major *E,E* conformers could be distinguished and, due to the rapid weakening of the spectra at high temperatures, exchange broadening could not be observed.

Table 2

ESR Parameters of 1,3-Disubstituted Pentadienyl Radicals.



Radical	T(K)	H_1^{anti}	H_1^{syn}	$H_{2,4}$	H_5^{anti}	H_5^{syn}	H^{Other}
R=H	450	9.8	9.3	3.8	9.8	9.3	10.9(CH_3)
R=H	289	9.7	9.3	3.2	9.7	9.3	10.2(CH_3)
R=OH	239	–	9.2	3.0	9.2	9.2	9.3(CH_3), 0.8(OH)
R=$OSiMe_3$	239	–	9.1	3.1	9.6	9.6	9.3(CH_3)

3-*iso*-Propylpenta-1,4-diene and 3-*tert*-butylpenta-1,4-diene were reacted with *tert*-butoxyl radicals, but no ESR signals were obtained in the accessible temperature range of the spectrometer.

2.9 Stability Of Pentadienes.

The $\Delta H_f^o(PD^\bullet)$ values and the bond dissociation energies of the bis-allylic hydrogens in penta-1,4-diene published elsewhere are in good agreement with the values obtained in this work (see Table 3).

Table 3

Thermodynamic Data for Pentadienyl and Related Radicals[a]

Radical	Method	$DH^o(R–H)$	$\Delta H_f^o(R^•)$	SE^{MeH}[m]	SE^{MH}	SE^{ESR}	Ref.
PD	GPP[c]	[76.8]	49.9[j]	28.3	19.5	–	1,2
PD	GPP[d]	76.6	49.7	28.5	19.6	–	1,2
PD	PAC[e]	76.4	[49.9][k]	28.5	19.6	–	n
PD	AE[f]	[76.5]	49.6	28.6	19.7	–	n
PD	ESR[g]	–	–			25.0	n
3-MePD	PAC[e]	76.6	[43.6][l]	28.5			n
3-MePD	ESR[g]	–	–			25.0	n
3-HOPD	PAC[e]	69.0		36.1			n
Cp	RB[h]	81.2	60.9	[23.9]			16
Ch[b]	ESR[i]	73.0	64.8	[32.1]			18
$CpMe_5$	ESR[i]	[67.2]	7.39	37.9	27.2		n

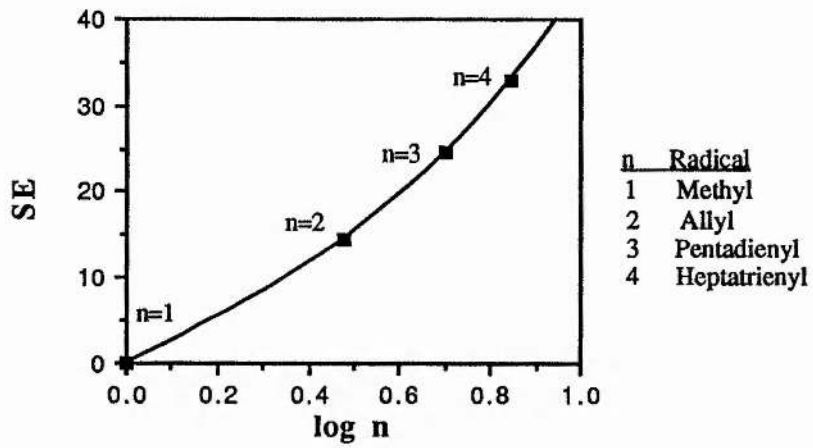
(a) All data in kcal mol^{-1}, value in parenthesis indicates derived data. (b) Cycloheptatrienyl radical. (c) Gas phase pyrolysis of hexa-1,3-diene. (d) Gas phase pyrolysis of 3-methylpenta-1,4-diene. (e) Photoacoustic calorimetry. (f) Appearance energy. (g) ESR study of internal rotation . (h) Radical Buffer. (i) ESR Dimer–Radical equilibrium. (j) Including 4 kcal mol^{-1} for conjugation in hexa-1,3-diene. (k) DH_f^o(Penta-1,4-diene) taken as 25.2 kcal mol^{-1}. (l) ΔH_f^o(3-methylpenta-1,4-diene) taken as 19.1 kcal mol^{-1}. (m) Assuming $DH^o(CH_3–H)$ = 105.1 kcal mol^{-1}. (n) This work.

The averages of gas phase pyrolysis, appearance energy, photoacoustic calorimetry and ESR measurements, which all give very similar results are;

$\Delta H_f^o(PD^•)$ = 49.8±1.0 kcal mol^{-1}.

$DH^o[(CH_2=CH)_2CH–H]$ = 76.6±1.0 kcal mol^{-1}.

The SE(PD•) values were compared with other polyenyl radicals in order to observe any relationship between SE and the extent of electron delocalisation. However, data are limited and SE^{MeH} values are only available for the first three members of the series and SE^{ESR} values up to four members (heptatrienyl).[96] It has been reported that for several series of carbocations the SE varies linearly with the logarithm of the number of atoms.[62] The SE data for polyenyl radicals was therefore plotted against log n, where n is the number of carbon atoms.



The results in Table 3 show that a 3-methyl substituent has very little effect on the SE of pentadienyl radicals. This is in agreement with results for allyl radicals which showed that SE(allyl) was unaffected by alkyl substituents.[97] The 3-hydroxy substituent caused a decrease in DH^{o}(C–H) of about 7 kcal mol^{-1} and an equivalent increase in SE(PD•). This is not unexpected as OH is known to have a stabilising effect in allyl radicals.[74]

The SE of cyclic systems is greater than in linear systems because in cyclic polyenyl radicals a greater overlap of the π-orbitals allows a greater degree of delocalisation and hence an increase in stability. Note, however, that whilst the cyclopropenyl cation is delocalised, the cyclopropenyl radical is non-delocalised and hence does not gain this extra stabilisation.

From the Table it can be seen from the values of SE^{MeH} (pentamethyl-cyclopentadienyl) and SE^{MeH} (cycloheptatrienyl) that these radicals are more stable than any of the linear pentadienyl radicals. The data for the cyclopentadienyl radical, however, is somewhat dubious. The value quoted for $DH^{o}(R–H)$ in McMillan and Goldens 1982 review[74] appears to be incorrect. Using the value of 81.2 kcal mol^{-1} from Furuyama[11], which was obtained by the gas-phase iodination method, the calculated SE^{MeH} of 23.9 kcal mol^{-1} is rather low compared to the cycloheptatrienyl radical and is lower than that of the linear pentadienyl radicals. In any future work it would well worth re-checking $DH^{o}(R–H)$ for the cyclopentadienyl radical to determine whether the current literature data is correct.

The value of SE^{MeH} for the pentamethylcyclopentadienyl radical is much larger than that of the cycloheptatrienyl radical. This may be explained by the fact that additional stability is achieved through hyperconjugation from the five methyl substituents on the cyclopentadienyl ring.

BDE and ΔH_f^{o} values of these hydrocarbon radicals in hydrocarbon solvents do not differ greatly from those measured in the gas phase (Table) and it may be concluded that solvent effects are negligible.

2.10 Experimental.

^{1}H NMR were recorded using a Varian EM-360 NMR Spectrometer (60 MHz), a Bruker WP80 NMR Spectrometer (80 MHz) and a Bruker AM300 NMR Spectrometer (300 MHz). ^{13}C NMR were recorded using a Bruker AM300 NMR Spectrometer (75 MHz) using DEPT-135 pulse techniques to assign peaks where necessary. Samples were normally run in $CDCl_3$ using tetramethylsilane as an internal standard.

IR spectra were recorded using a Perkin-Elmer 1420 Infra-Red Spectrometer and were run as liquid film samples.

ESR spectra were recorded using a Bruker ER200D ESR Spectrometer with photolysis from a 500 W super-pressure Hg arc lamp. Samples were normally run in *tert*-butylbenzene and were degassed before analysis.

GC/MS were run on a Finnigan Incos 50 Quadrupole Mass Spectrometer using a Hewlet-Packard HP5890 Gas Chromatograph. Preparative GLC were carried out on a Pye-Unicam 105 Chromatograph

1,1',2,2',3,3',4,4',5,5'-Decamethylbis(cyclopentadienyl).[35]

To a solution of 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (1.0 g; 7.34 mmol) in dry ether (28 cm^3) was added, under N_2, a solution containing 9.3 mmol of methyl lithium (6.2 cm^3 of a 1.5 M solution in hexane). The mixture was then refluxed overnight, to form a white suspension of lithium pentamethylcyclopentadienide. The lithium pentamethylcyclopentadienide solution was allowed to cool and freshly prepared copper (I) chloride (0.65 g; 6.57 mmol) and dry ether (28 cm^3) were added. The mixture was stirred under nitrogen for 5 hours. After this time, the solution had gone black and a thin copper mirror was observed on the walls of the flask. The solution was evaporated to give a bright green solid. Water and ether were added to the solid and the ether extracted, after which the aqueous layer was further extracted with ether (x3). The combined ether layers were dried (Na_2SO_4 anhyd.) and evaporated to give a yellow oil which crystallised out. The crude bis(cyclopentadienyl) was re-

crystallised from methanol to yield a white solid. M.pt. 48-49 °C. Found: C 88.50%, H 11.29%. Calc. for $C_{20}H_{30}$: C 88.82%, H 11.18%; δ_H 1.13 (6H, s, 1,1'- CH_3), 1.66 & 1.72 (24H, 2 s, 2,2'- ,3,3'- ,4,4'- ,5,5'- CH_3).

Copper (I) Chloride.[36]

Copper (II) sulphate pentahydrate (15.0 g; 60.1 mmol) and sodium chloride (3.9 g; 66.7 mmol) were dissolved in water (53.6 cm^3), warming gently to aid dissolution. To this, a solution of sodium metabisulphite (3.6 g; 18.9 mmol) in water (38.6 cm^3) was added over *ca.* 5 min. with constant stirring. The solution was then decanted to leave the white copper (I) chloride which had precipitated. The white solid was washed several times with water through which a little sulphur dioxide had been bubbled. The solid was then collected on a Buchner funnel and washed with glacial acetic acid, before drying in an oven at 100 °C.

3-Bromohex-3-ene.[39]

Through a stirred solution of hex-3-yne (2.0 g; 0.024 mol) in pentane (25 cm^3) at 0 °C, was bubbled hydrogen bromide gas. The gas was bubbled for about 40 min. until the solution became pale orange, after which the solvent was distilled off and the residue was vacuum distilled to give 3-bromohex-3-ene (bpt 58 °C/ 20 mmHg; Lit.[39] 47-48 °C/ 23 mmHg). Yield 2.1 g; 54%. δ_H 1.15 (6H, t, CH_3), 1.68-2.74 (4H, m, CH_2), 5.64 (1H, br t, CH).

Attempted Preparation of 1,1',2,2',3,3',4,4',5,5'-Decaethylbis(cyclopentadienyl).

To a well stirred solution of cut up lithium wire (0.49 g; 0.071 mol) in dry ether (70 cm^3) under argon, was added a small portion of 3-bromohex-3-ene (5.7 g; 0.035 mol). After the reaction began, the remainder of the bromide was added at a sufficient rate to maintain gentle reflux. It was then stirred for 1 hr. after which time any unreacted lithium was removed. A solution of methyl propionate (1.57 g;

0.018 mol) in dry ether (2 cm^3) was added dropwise. An exothermic reaction occurred and the solution became milky. The solution was then poured onto saturated ammonium chloride solution (45 cm^3). The aqueous layer was then removed and was adjusted to *ca.* pH 9 with dilute hydrochloric acid, before re-extracting with ether. The combined ether layers were dried (Na_2SO_4 anhyd.) and evaporated to *ca.* 3-6 cm^3. The concentrate was then added to a solution of *p*-toluenesulphonic acid in dry ether (7 cm^3). No exothermic reaction occurred, not even after stirring for several minutes so a few drops of concentrated sulphuric acid were cautiously added. The reaction mixture became warm and water was observed to come out of solution. After stirring for 5 min., the solution was poured onto saturated sodium hydrogen carbonate solution (45 cm^3) and the excess acid was neutralised by addition of solid sodium carbonate. The ether layer was then removed and the aqueous was re-extracted (x3). The combined ether layers were dried (Na_2SO_4 anhyd.), evaporated and distilled by kugelrohr (153 ^oC/ 14 mmHg). The ^1H NMR was not well resolved, but the formtion of the exocyclic methylene compound was suspected. δ_H 0.79-1.15 and 1.93-2.34 (Complex, and probably due to the ethyl substituents), 1.72 (3H, d, CH_3), 5.70 (1H, q, CH).

m/z 206 (M^+, 30), 191 (28), 177 (100), 163 (9), 149 (27), 135 (15), 121 (31), 107 (20), 93 (25), 77 (11).

1,1,2,3,4,5,6,7-Octamethoxycarbonylcyclohepta-3,5-diene.[41]

Dimethyl acetylenedicarboxylate (15.0 g; 0.106 mol) and dimethyl malonate (4.7 g; 0.036 mol) were stirred together in dry ether (25 cm^3). To this, a mixture (1:1; w:w) of pyridine and glacial acetic acid (1.0 g) was added dropwise. The solution rapidly went from yellow through red to dark brown and was accompanied by a slow exothermic reaction which eventually led to the solution refluxing. After the reaction subsided it was refluxed on an oil bath for a further 2 hr. After this time a solid precipitated out of the solution which was then allowed to cool. The solid was filtered and washed with ether before being dissolved in methanol. Both the 3,5- and

4,6-dienes formed in the reaction and the 4,6-diene remained insoluble in the methanol and was filtered off. The filtrate was evaporated to a minimum and the 3,5-diene allowed to crystalise out on standing. The solid was filtered under suction, washed with a little ether and pumped dry to give the product. Yield 4.4 g; 23%

Potassium Pentamethoxycarbonylcyclopentadiene.[41]

A mixture of 1,1,2,3,4,5,6,7-octamethoxycarbonylcyclohepta-3,5-diene (4.4 g; 8.0 mmol) and potassium acetate (7.26 g; 0.074 mol) in water (22 cm^3) was refluxed for 2 hr. The hot solution was then filtered and evaporated to a minimum, upon which the product crystallised out on standing. The product was filtered and washed with water and a little ether before pumping dry. It was then dried in a drying pistol (130 °C/ 1 mmHg). Yield 1.14 g; 36%

1,1'2,2'3,3'4,4'5,5'-Decamethoxycarbonylbis(cyclopentadienyl).[42]

To a stirred solution of potassium pentamethoxycarbonylcyclopentadienide (0.5 g; 1.27 mmol) in 50% water/methanol (3 cm^3) was added a solution of ceric ammonium nitrate (0.70 g; 1.27 mmol) in 50 % methanol/water (3.75 cm^3). On addition, a cloudy white precipitate formed. The solution was stirred for 30 min., filtered, washed with ice-cold 50% methanol/water and pumped dry to give a pure white solid, which was re-crystallised from methanol (x3). Yield 0.4 g; 44%. M.pt. 170 °C;Lit.[42] 175-176 °C.(Lit.[42]) δ_H 3.69 (6H, s, 1,1'- CH_3), 3.81 & 3.83 (24H, 2 s, 2,2'-, 3,3'- 4,4'- 5,5'- CH_3). (Lit.[42]) δ_C 53.33 (CH_3), 54.42 (CH_3), 67.88 (saturated ring C), 139.55 (unsaturated ring C), 141.21 (unsaturated ring C), 161.67 (carbonyl C), 164.24 (carbonyl C). (Lit.[42]) *m/z* 710 (M^+, 9), 679 (1), 666 (6), 651 (3), 622 (4), 607 (4), 576 (4), 531 (7), 517 (3), 471 (4), 457 (4), 409 (4), 395 (4), 327 (22), 299 (22), 293 (59).

Thermal rearrangement Of 1,1,'2,2',3,3',4,4',5,5'-decamethoxy-carbonylbis(cyclopentadienyl).

A small amount of 1,1,'2,2',3,3',4,4',5,5'-decamethoxycarbonylbis(cyclopentadienyl) was heated in *tert*-butylbenzene at 120-140 °C until a red/brown colour developed. The solvent was then removed on a rotary evaporator and the final traces were removed using a rotary pump. Deuteriochloroform was added to the residue. δ_H.3.71 (12H, s, CH_3), 3.81 (6H, s, CH_3), 3.83 (6H, s, CH_3), 3.87 (6H, s,CH_3). δ_C 53.95 (CH_3), 54.20 (CH_3), 54.45 (CH_3), 55.55 (CH_3), 133.74 (unsaturated ring C), 142.54 (unsaturated ring C), 158.98 (carbonyl C), 161.22 (carbonyl C). *m/z* 710 (M^+, 6), 667 (74), 652 (12), 636 (14), 577 (9), 546 (16), 532 (35), 506 (7), 499 (12), 488 (9), 471 (7), 458 (11), 426 (12), 414 (12), 396 (15), 384 (8), 369 (9), 355 (10), 293 (20).

Activated zinc.[50]

Zinc dust was activated by washing successively with 2% hydrochloric acid, distilled water, 95% ethanol, acetone and dry ether. It was then dried in an oven. It was found that in order to obtain the best results in the Reformatsky reaction the reagents should be added to the zinc when it had just been removed from the oven and is still hot.

Ethyl 3-methyl-3-hydroxypent-4-enoate.[51]

A portion of a solution of ethyl bromoacetate (60.0 g; 0.359 mol) and methyl vinyl ketone (25.0 g; 0.357 mol) in dry ether (175 cm^3) was added to activated zinc (42.0 g; 0.642 mol), with a crystal of iodine. After the initial exothermic reaction began, the remainder of the solution was added dropwise with stirring (mechanical stirrer) keeping the mixture gently refluxing. After addition, the solution was maintained at reflux by heating on an oil bath for a further 1.5 hr. After cooling, the mixture was filtered to give a yellow solution. Acetic acid (273 cm^3; 1.7 M) was added and the aqueous phase was saturated with ammonium chloride. The organic phase was

separated and the aqueous was further extracted with ether (x2). The combined organic layers were washed (sat. $NaHCO_3$ aq., water), dried (Na_2SO_4 anhyd.) and evaporated. The crude product was distilled on a spinning band distillation column (78 °C/ 14 mmHg; Lit.[51] 82 °C/ 15 mmHg). Yield 30.0 g; 53%. δ_H 1.28 (3H, t, $CH_2\underline{CH_3}$), 1.33 (3H, s, CH_3), 2.56 (2H, s, CH_2), 3.80 (1H, s, OH), 4.20 (2H, q, $\underline{CH_2}CH_3$), 4.98-5.40 (2H, m, CH_2), 5.98 (1H, dd, CH). δ_C 13.94 (CH_3), 27.88 (CH_3), 45.00 (CH_2), 60.48 ($\underline{CH_2}CH_3$), 70.97 (C), 112.30 (CH_2), 143.15 (CH), 171.94 (C-carbonyl). (Lit.[51]) IR (liquid film) υ cm^{-1} 3490 (OH), 3080 (*sp* C–H), 2975 (sp^3 C–H), 1715 (C=O), 1640 (C=C), 1200 (C–O), 923 ($CH=CH_2$).

Ethyl 3-methyl-3-acetoxypent-4-enoate.[51]

A suspension of *N*-acetylpyridinium chloride was prepared by the gradual addition of acetyl chloride (50.0 g; 0.637 mol) in benzene (325 cm^3) to a solution of dry pyridine (100.0 g; 1.264 mol) in benzene (325 cm^3). To this stirred suspension, ethyl 3-methyl-3-hydroxypent-4-enoate (50.0 g; 0.316 mol) was added slowly and the resulting mixture was heated at 80 °C (gentle refluxing) overnight. The mixture was allowed to cool and the solid removed by filtration. The benzene solution was washed (dil. HCl, sat.$NaHCO_3$ aq.), dried (Na_2SO_4 anhyd.) and evaporated. The product was distilled on a spinning band distillation column (98-102 °C/ 14 mmHg; Lit.[51] 104-105 °C/ 13 mmHg). Yield 43.0 g; 68%. δ_H 1.27 (3H, t, $CH_2\underline{CH_3}$), 1.62 (3H, s, CH_3), 2.02 (3H, s, $COCH_3$), 2.96 (2H, s, CH_2), 4.12 (2H, q, $\underline{CH_2}CH_3$), 5.05-5.50 (2H, m, CH_2), 6.20 (1H, dd, CH). (Lit.[51]) IR (liquid film) υ cm^{-1} 3080 (*sp* C–H), 2975 (sp^3 C–H), 1733 (C=O), 1648 (C=C), 1370 (sp^3 C–H), 860 (sp^2 C–H).

Ethyl 3-methylpenta-2,4-dienoate.

Ethyl 3-methyl-3-acetoxy-pent-4-enoate (*ca.* 12 g portions) was subjected to flash vacuum pyrolysis at 570 °C/ 10^{-2} mmHg. The products were collected in a cooled trap (liq.N_2). The combined products from several runs were dissolved in methylene

chloride and washed with sat. $NaHCO_3$ solution to remove acetic acid. The solution was dried (Na_2SO_4 anhyd.) and distilled to give a mixture of the *trans*- and *cis*-isomers in a good yield. The ^1H NMR spectra of the two isomers overlapped extensively, (Lit.[98]) δ_H 1.26 (3H, t, CH_3 *cis/trans*-overlap), 2.00 (3H, s, CH_3 *cis*), 2.28 (3H, s, CH_3 *trans*), 4.18 (2H, q, CH_2 *cis/trans*-overlap), 5.02-5.80 (2H, m, CH_2 *cis/trans*-overlap), 6.35-6.48 (1H, m, CH *cis/trans*-overlap), 7.83 (2H, dd, CH *cis* , J = 19, 16 Hz). The ^{13}C spectra were resolvable: *trans*-isomer; (Lit.[98]) δ_C 14.23 ($CH_2\underline{C}H_3$), 20.00 (CH_3), 59.64 ($\underline{C}H_2CH_3$), 117.98 (CH), 119.29 (CH_2), 140.06 (CH), 151.79 (C), 166.67 (C-carbonyl); *cis*-isomer, δ_C 12.86 ($CH_2\underline{C}H_3$), 24.76 (CH_3), 60.71 ($\underline{C}H_2CH_3$), 119.82 (CH_2), 120.18 (CH), 133.93 (CH), 150.64 (C), 165.89 (C-carbonyl). (Lit.[98]) *m/z* 140 (M^+, 51), 112 (70), 111 (68), 97 (38), 95 (100), 67 (75), 55 (25), 43 (27), 41 (84), 39 (62).

3-Methylpenta-2,4-dien-1-ol

A solution of ethyl 3-methylpenta-2,4-dienoate (6.0 g; 61.1 mmol) in dry ether (90 cm^3) was added dropwise to a suspension of lithium aluminium hydride (1.2 g; 31.6 mmol) in dry ether (90 cm^3) under N_2 at -5 °C. After stirring at room temperature for 1 hr., water was carefully added to destroy excess lithium aluminium hydride. The ether layer was decanted, and conc. HCl was added to the remaining aqueous layer, which was subsequently extracted with more ether. The combined ether layers were washed with water, dried (Na_2SO_4 anhyd.), and evaporated. The alcohol was distilled at 88 °C/ 14 mmHg (Lit.[51] 75-76 °C/ 15 mmHg). Yield 3.42 g; 57%. *Trans*-isomer; some of the peaks overlapped with the *cis*- isomer and could not be resolved, (Lit.[99]) δ_H 1.77 (3H, s, CH_3), 4.30 (2H, d, $\underline{C}H_2OH$), 5.69 (1H, br t, CH), 6.40 (1H, dd, CH); δ_C 11.88 (CH_3), 59.39 (CH_2), 113.19 (CH_2), 130.42 (CH), 138.34 (C), 140.72 (CH). *Cis*-isomer; δ_H 1.87 (3H, s, CH_3), 4.30 (2H, d, $\underline{C}H_2OH$), 5.18 (1H, br d), 5.59 (1H, br t, CH), 5.29 (1H, br d), 6.74 (1H, dd, CH); δ_C 20.0 (CH_3), 58.3 (CH_2), 115.5 (CH_2), 128.2 (CH), 132.6 (CH), 135.2 (C) (Lit.[99]) *m/z* 98 (M^+, 33), 83 (63), 79 (28), 69 (83), 67 (69), 55 (68), 53 (58), 43 (48), 41 (100), 39 (95).

1-Trimethylsilyloxy-3-methylpenta-2,4-diene

Trimethylsilyl chloride (1.1 g; 10.1 mmol) in 40-60 °C petroleum ether (20 cm^3) was added dropwise to 3-methylpenta-2,4-dien-1-ol (1.0 g; 10.2 mmol) and pyridine (0.80 g; 10.1 mmol) in 40-60 °C petroleum ether (20 cm^3). The solution was stirred for 0.5 hr, filtered and distilled at 73 °C/ 14 mmHg to give the product as a mixture of isomers.Yield 1.0 g; 58%. δ_H *trans*- isomer 0.12 (9H, s, $Si(\underline{CH_3})_3$), 1.76 (3H, s, CH_3), 4.29 (2H, d, CH_2OSi), 5.12-5.34 (2H, m, CH_2), 5.52 (1H, br t, CH), 6.66-6.83 (1H, m, CH). The *cis*- isomer overlapped considerably with the *trans*-isomer except for 1.79 (3H, s, CH_3) and 5.52 (1H, br t, CH). δ_C *trans*-isomer -0.24 ($OSi(CH_3)_3$, 11.90 (CH_3), 69.76 (CH_2), 112.50 (CH_2), 131.55 (CH), 134.88 (C), 141.19 (CH). *cis*-isomer,similar except for 11.73 (CH_3), 113.33 (CH_2), 141.07 (CH). The ^1H NMR spectrum indicated the *trans*/*cis*-ratio was *ca.* 2.4:1; *m*/*z* 170 (M^+, 11), 155 (50), 80 (25), 75 (96), 73 (100), 20 (10), 59 (12), 53 (13).

5-Bromo-3-methylpenta-1,3-diene [52]

Phosphorus tribromide (1.1 g; 4.1 mmol) was added dropwise to a solution of 3-methylpenta-2,4-dien-1-ol (1.0 g; 10.2 mmol) and pyridine (0.04 g; 0.51 mmol) in dry ether (20 cm^3) cooled to -5 °C, in an ice/salt bath. The mixture was stirred cold for 20 min then ice/water (20 cm^3) was added. The ether was decanted and the aqueous phase was extracted with more ether. The combined ether layers were washed (water, sat. $NaHCO_3$ aq., sat. NaCl aq.), dried (Na_2SO_4 anhyd.) and evaporated. The product was distilled at 52 °C/ 14 mmHg (Lit.[52] 45 °C/ 10 mmHg) to give 0.75 g; 45% of the *trans*/*cis*-isomer mixture. Attempts to separate them by preparative GLC were unsuccessful. The ^1H NMR spectra overlapped considerably; *trans*-isomer: δ_H 1.85 (3H,s, CH_3), 4.12 (2H,d, CH_2Br), 5.03-5.63 (2H,m,), 5.80 (1H,br t, CH), 6.40 (1H,dd, CH). The *cis*-isomer had similar shifts except for 1.90 (3H,s, CH_3), 6.80 (1H,dd, CH). The *trans*/*cis*-ratio was 2.0:1. δ_C (*trans*-isomer) 11.33 (CH_3), 29.03 (CH_2), 114.85 (CH_2), 126.85 (CH), 139.64 (C), 140.12 (CH); *cis*-isomer 19.82 (CH_3), 27.82 (CH_2), 117.03 (CH_2), 124.79 (CH), 131.82 (CH), 138.12 (C);

m/z 162, 160 (M^+,5), 81 (100), 79 (32), 66 (10), 53 (37), 41 (49), 39 (28).

3,8-Dimethyldeca-1,3,7,9-tetraene.

A portion of a solution of 5-bromo-3-methylpenta-1,3-diene (4.0 g; 24.8 mmol) in dry ether (100 cm^3) was added to dry magnesium turnings (0.8 g; 32.9 mmol) along with a crystal of iodine, under N_2. The mixture was heated gently to start the reaction and the remainder of the pentadiene solution was added at such a rate to maintain gentle reflux. After addition the mixture was maintained at reflux for 1.5 hr with an oil bath. Copper (I) chloride (0.3 g; cat.) and a further solution of 5-bromo-3-methylpenta-1,3-diene (4.0 g; 24.8 mmol) in dry ether (50 cm^3) was added and the mixture refluxed for 5 hr. The solution was allowed to cool and was poured onto cold ammonium chloride solution (100 cm^3). The ether was extracted and the aqueous re-extracted further. The combined ether layers were washed.(water), dried (Na_2SO_4 anhyd.), evaporated and distilled. (50 °C/ 1 mmHg). Yield 3.1 g; 77%. The product formed as a mixture of $C_{12}H_{18}$ isomers, which were separated by preparative GLC. (12' column packed with 20% Carbowax 20 M maintained at 115 °C). The isomers were identified as *cis*-3,6-dimethyl-6-ethenyl-octa-1,3,7-triene (1.6%) δ_H 1.09 (3H, s, CH_3), 1.84 (3H, s, CH_3), 2.29 (2H, d, CH_2), 4.94-5.10 (6H, m, CH_2), 5.82 (2H, dd, CH), 6.74 (1H, dd, CH). *trans*-3,6-dimethyl-6-ethenyl-octa-1,3,7-triene (21.9%) δ_H 1.08 (3H, s, CH_3), 1.74 (3H, s, CH_3), 2.27 (2H, d, CH_2), 4.91-5.12 (6H, m, CH_2), 5.46 (1H, t, CH), 5.82 (2H, dd CH), 6.37 (1H, dd, CH); δ_C 12.00 (CH_3), 23.03 (CH_3), 39.15 (CH_2), 43.77 (C), 110.30 (CH_2), 112.36 (CH_2), 129.27 (CH), 135.70 (C), 141.82 (CH), 145.52 (CH); *m/z* 162 (M^+, 1), 147 (4), 133 (1), 119 (2), 106 (4), 91 (3), 81 (100), 79 (46), 77 (11), 65 (9), 53 (37), 41 (44). *cis-trans*-3,8-dimethyldeca-1,3,7,9-tetraene (10.6%) δ_H 1.73 (3H, s, CH_3), 1.82 (3H, s, CH_3), 2.25 (4H, m, CH_2), 5.01 (2H, dd, CH_2), 5.16 (2H, dd, CH_2), 5.40 (1H, br t, CH),5.49 (1H, br t, CH), 6.37 (1H, dd, CH), 6.77 (1H, dd, CH); δ_C 11.67 (CH_3), 19.55 (CH_3), 27.16 (CH_2), 28.36 (CH_2), 110.66 (CH_2), 113.52 (CH_2), 130.54 (CH), 132.39 (CH), 133.58 (C), 134.66 (C), 141.79 (CH).*trans-trans*-3,8-dimethyldeca-1,3,7,9-tetraene (65.9%).

δ_H 1.74 (6H, s, CH_3), 2.24 (4H, m, CH_2), 5.01 (4H, dd, CH_2), 5.48 (2H, br t, CH), 6.36 (2H, dd, CH); δ_C 11.43 (CH_3), 28.18 (CH_2), 110.60 (CH_2), 132.09 (CH), 134.18 (C), 141.31 (CH); *m/z* 162 (M^+, 5), 147 (4), 133 (2), 119 (3), 106 (10), 91 (4), 81 (100), 79 (51), 77 (14), 65 (13), 53 (51), 41 (67).

2,6-Dimethylhepta-3,5-dien-4-ol.

To a solution of lithium aluminium hydride (1.5 g; 39.5 mmol) in dry ether (150 cm^3) at 0 °C under N_2 was added a solution of 2,6-dimethylhepta-2,5-dien-4-one (phorone) (15.0 g; 0.109 mol) in dry ether (100 cm^3) dropwise. The mixture was stirred overnight at room temperature. The excess lithium aluminium hydride was cautiously decomposed with water and the clear ether layer was removed. The aqueous etherate was broken up with dil. HCl and re-extracted with ether (x2). The combined ether layers were washed (sat. $NaHCO_3$ aq., water), dried (Na_2SO_4 anhyd.) and evaporated to give the alcohol which was distilled by kugelrohr to give a clear colourless liquid. Yield 6.0 g; 39%. (Lit.[100]) δ_H 1.28 (12H, s, CH_3), 5.40-5.98 (2H, m, CH), 6.06-6.54 (1H, m, CH).

Attempted Preparation of 6-Bromo-2,6-dimethylhepta-2,4-diene.

To an ice-cold solution of hydrobromic acid (48%; 2.65 cm^3) was added 2,6-dimethylhepta-2,6-dien-4-ol (2.0 g; 14.3 mmol) dropwise, keeping the temperature at 0 °C. The resultant orange solution was allowed to warm to room temperature and was stirred for 2.5 hr. The dark brown liquid was then extracted with ether and separated. The aqueous was further extracted and the combined ether layers were then washed (H_2O), dried (Na_2SO_4 anhyd.) and evaporated to give a brown liquid.

The sample became black and decomposed within about 20 min. at room temperature. This rapid decompostion prevented accurate spectral confirmation of the product.

2,7-Dimethyl-4,5-bis(2-methylprop-1-enyl)octa-2,6-diene.

Titanium (III) chloride (26.29 g; 0.170 mol) and lithium aluminium hydride (2.17 g; 0.057 mol) were stirred in dry dimethoxyethane (100 cm^3) for 30 min. A solution of 2,6-dimethylhepta-2,5-dien-4-ol (8.00 g; 0.057 mol) in dry dimethoxyethane (40 cm^3) was added dropwise to the slurry and the resulting mixture was refluxed for 24 hr. under N_2. After allowing to cool, water (100 cm^3) was cautiously added and the mixture was extracted with ether (x 3). The combined ether layers were washed (water, sat. NaCl aq.), dried (Na_2SO_4 anhyd.), evaporated and distilled to give a pale yellow liquid (40 °C/ 1 mmHg). The product was not the expected 'middle to middle' dimer, but the product of 'middle to end' dimerisation, namely 2,6,6,9-tetramethyl-7-(2-methylprop-1-enyl)-deca-2,4,8-triene. δ_H 0.94 (6H, s, CH_3), 1.59 (6H, s, CH_3), 1.68 (6H, s, CH_3), 1.77 (6H, s, CH_3), 2.95 (1H, t, CH), 5.00 (2H, d, CH), 5.60 (1H, d, CH), 5.70 (1H, d, CH), 6.10 (1H, dd, CH). δ_C 18.29 (CH_3), 18.36 (CH_3), 25.44 (CH_3), 25.96 (CH_3), 26.12 (CH_3), 40.49 (C), 47.49 (CH), 123.14 (CH), 125.44 (CH), 125.73 (CH), 130.81 (C), 132.56 (C), 140.22 (CH). *m/z* 246 (M^+, 10), 190 (5), 149 (5), 123 (52), 107 (47), 81 (29), 69 (100).

2,6-Dibenzylidene-4-*tert*-butylcyclohexanone.[76]

4-*tert*-Butylcyclohexanone (65.5 g; 0.425 mol) and benzaldehyde (104.0 g; 0.980 mol) were dissolved in ethanol (283 cm^3). A solution of sodium hydroxide (1.45 g; 36.3 mmol) in water (13.6 cm^3) was added to the pale yellow solution which warmed and became opaque. A solution of 2 M sodium hydroxide was then slowly added dropwise until a bright yellow precipitate came out of solution. The solid was filtered under vacuum. Sodium hydroxide solution was added to the filtrate and the latter allowed to stand overnight, after which more solid had precipitated out. The combined solid samples were then dried in an oven. Yield 132.0 g; 94%.

3-*tert*-Butylpentane-1,5-dioic acid.[76]

A stream of ozone in oxygen was passed through a suspension of 2,6-dibenzylidene-4-*tert*-butylcyclohexanone (44.0 g; 0.13 mol) in glacial acetic acid (460 cm^3). After several hours the suspension dissolved to give a yellow solution. Ozone was continually passed through the solution until all the yellow colour had been discharged (which took several days). Water (60 cm^3) and 30% hydrogen peroxide solution (67.5 cm^3) were added and the mixture refluxed for 3 hr. The solvent was removed on a rotary evaporator to give a yellow liquid which solidified on cooling to room temperature. The product was a mixture of the diacid (1 part) and benzoic acid (2 parts) and separation was achieved through esterification.

Diethyl 3-*tert*-butylpentane-1,5-dioate.[76]

To the acid mixture prepared from above, was added benzene (75 cm^3), dry ethanol (75 cm^3) and conc. sulphuric acid (1.5 cm^3). The mixture was then azeotropically esterified by refluxing the mixture and removing any water formed by a Dean and Stark trap. The mixture was then evaporated and ether and water were added. After extraction, the aqueous was repeatedly extracted with more ether. The combined ether layers were washed (sat. $NaHCO_3$ aq., water), dried (Na_2SO_4 anhyd.), evaporated and distilled to give ethyl benzoate (75 °C/ 1 mmHg; Lit.[76] 49 °C/ 0.13 mmHg) and diethyl 3-*tert*-butylpentane-1,5-dioate (118 °C/ 1 mmHg; Lit.[76] 80 °C/ 0.13 mmHg). Yield 54.8 g; 56% (overall from 2,6-dibenzylidene-4-*tert*-butylcyclohexanone). (Lit.[77]) δ_H 0.93 (9H, s, $C(\underline{CH_3})_3$), 1.25 (6H, t, $\underline{CH_3}CH_2$), 1.93-2.71 (5H, m, $\underline{CH}(CH_2)_2$), 4.12 (4H, q, $CH_3\underline{CH_2}$).

3-*tert*-Butylpentane-1,5-diol diacetate.

To 3-*tert*-butylpentane-1,5-diol (5.0 g; 31.2 mmol) at 100 °C was added acetic anhydride (3.51 g; 34.4 mmol) dropwise. The mixture was then refluxed for 4.5 hr. After cooling the mixture was distilled by kugelrohr to give the pure diacetate (143 °C/ 1 mmHg). Yield 5.8 g; 77%. δ_H 0.88 (9H, s, $C(\underline{CH_3})_3$), 1.03-1.94 (5H, m,

$\underline{CH}(\underline{CH_2})_2$), 2.04 (6H, s, CH_3), 4.05 (4H, br t, CH_2).

3-*tert*-Butylpentane-1,5-diol ditosylate.[77]

p-Toluenesulphonyl chloride (2.4 g; 12.6 mmol) was added to a solution of 3-*tert*-butylpentane-1,5-diol (1.0 g; 6.0 mmol) in dry pyridine (7 cm^3) at 0 °C. The mixture was stirred for 20 min. then allowed to stand at 0 °C for 24 hr. The mixture was then added to 20% HCl (21 cm^3), extracted with ether (x 3), washed (sat. $NaHCO_3$ aq.), dried (Na_2SO_4 anhyd.) and evaporated to dryness to give the solid ditosylate.

(Lit.[77]) δ_H 0.74 (9H, s, $C(\underline{CH_3})_3$); 0.93-2.08 (5H, m, $\underline{CH}(\underline{CH_2})_2$); 2.41 (6H, s, $ArCH_3$); 3.91 (4H, br t, CH_2O); 7.29 (4H, d, ArH); 7.77 (4H, d, ArH).

Sodium Selenocyanate.[88]

To a degassed solution of *N,N*-dimethylacetamide (DMAC) (150 cm^3) was added powdered selenium metal (15.8 g; 0.200 mol) and sodium cyanide (10.48 g; 0.214 mol), under N_2. The mixture was then heated to 110 °C until all the selenium metal had dissolved to give an almost colourless solution.

***o*-Nitrophenyldiazonium chloride.[88]**

A suspension of *o*-nitroaniline (27.62 g; 0.200 mol) in water (78 cm^3) and conc. hydrochloric acid (44 cm^3) was cooled to 2-3 °C. Sodium nitrite (14.94 g; 0.217 mol) in water (48 cm^3) was added to the orange suspension, keeping the temperature at 2-3 °C. It was then stirred for a further 1 hr at this temperature. 25% Sodium acetate solution (21 cm^3) was then added until the pH was *ca.*4.

***o*-Nitrophenylselenocyanate.[88]**

The diazonium compound was cooled to 0 °C and to this, the sodium selenocyanate solution was added dropwise. N_2 gas was evolved and a thick orange/yellow precipitate formed. It was stirred continuously and then left to stand

overnight. The solid was filtered off under reduced pressure, washed with water and pumped dry. It was then dried further in a vacuum desiccator over P_2O_5. The crude solid was dissolved in chloroform (200 cm^3) and passed through a column of silica gel (80 g; 80-120mesh; 0.125-0.250 mm). Excess chloroform was used to elute the product until about 800 cm^3 of chloroform had been eluted and had become colourless. After the solvent was evaporated the crude solid was re-crystallised from acetone and then re-crystallised from ethanol, filtered and dried in an oven to yield the pure product. Yield 16.5 g; 36%. M.pt. 138 °C (Lit.[88] 139-141 °C).

3-*tert*-Butyl-1,5-bis(*o*-nitrophenylseleno)pentane.

Tri-*n*-butylphosphine (6.07 g; 30.0 mmol) was added dropwise at room temperature to a stirred solution of 3-*tert*-butylpentane-1,5-diol (2.0 g; 12.5 mmol) and *o*-nitrophenyl selenide (6.8 g; 29.9 mmol) in dry THF (50 cm^3), under N_2. After an initial exothermic reaction, the solution became pale brown and was stirred overnight. A solid precipitated out of solution which was filtered off under reduced pressure. The THF solvent was removed from the filtrate to yield a viscous brown liquid.

3-*tert*-Butylpenta-1,4-diene.

To the previously prepared crude 3-*tert*-butyl-1,5-bis(*o*-nitrophenylseleno)-pentane in dry THF (25 cm^3) at 0 °C was added 30% hydrogen peroxide solution (22 cm^3; 0.25 mol) over 30 min. It was then stirred at 0 °C for 1.5 hr, then overnight at room temperature. The selenoxide solution had become clear red and was diluted with water before extracting with pentane (x3). The combined pentane extracts were washed (sat. $NaHCO_3$ aq. (x2), sat. NaCl aq., water, sat. NaCl aq.), dried (Na_2SO_4 anhyd.), filtered and passed through a short column of alumina (5 cm x 2 cm diameter) to remove the bulk of the selenium by-products. The solution was now yellow. The bulk of the pentane was distilled off and the remainder was re-filtered through alumina before continuing the distillation, to eventually give the diene in low yield (see later for spectra).

3-*tert*-Butylpentane-1,5-diol.

Diethyl 3-*tert*-butylpentane-1,5-dioate (54.8 g; 0.224 mol) in dry ether (255 cm^3) was added dropwise to a suspension of lithium aluminium hydride (10.0 g; 0.264 mol) in dry ether (200 cm^3) at 0 °C under N_2. The mixture was stirred for 15 hr at room temperature, excess lithium aluminium hydride was decomposed with water and conc. HCl, the aqueous phase was extracted with ether and the combined ether layers were dried ($MgSO_4$), evaporated and distilled (145 °C/ 1.5 mmHg; Lit.[77] 100 °C/ 0.4 mmHg; 132 °C/ 4.5 mmHg), to give the diol. Yield 17.5 g; 49%. (Lit.[77]) δ_H 0.88 (9H, s, CH_3), 1.05-2.02 (5H, m, $\underline{CH}(\underline{CH_2})_2$), 3.05 (2H, s, OH), 3.70 (1H, br t, CH).

3-*tert*-Butyl-1,5-dibromopentane

Methanesulphonyl chloride (23.6 g; 0.206 mol) was added dropwise to a solution of 3-*tert*-butylpentane-1,5-diol (15.0 g; 93.6 mmol) and triethylamine (19.0 g; 0.188 mol) in dry methylene chloride (300 cm^3) cooled to 0 °C under N_2. The solution was stirred for 1 hr., then washed (water, 2 M HCl, sat. NaCl aq.), dried (Na_2SO_4 anhyd.).and evaporated. The crude dimesylate was added to a solution of lithium bromide (32.7 g; 0.377 mol) in dry acetone (350 cm^3) which was refluxed for 15 hr. This solution was cooled, filtered and evaporated. Water was added to the residue which was then extracted several times with ether. The ether layers were washed with water, dried(Na_2SO_4 anhyd.) and evaporated. The residue was distilled (139 °C/ 1 mmHg), to give the dibromide. Yield 18.74 g; 70%. δ_H 0.90 (9H, s, CH_3), 1.25 (1H, m, CH), 1.63 (2H, m), 2.09 (2H, m), 3.44 (4H, m, CH_2). δ_C 24.93 (CH_2), 27.90 (C), 33.21 (CH_2), 34.95 (CH), 46.47 (CH_2Br).

3-*tert*-Butylpenta-1,4-diene.

The 3-*tert*-butyl-1,5-dibromopentane (1.7 g; 5.94 mmol) was heated to 195 °C and a stream of N_2 was bubbled through it. HMPT (2.3 g; 12.8 mmol) was added dropwise and the temperature was slowly raised to 210 °C. The diene was trapped out

of the N_2 stream in a dry ice/acetone bath. Pure diene was obtained by preparative GLC on a 12' column packed with 20% Carbowax 20 M maintained at 60 °C.

(Lit.[75]) δ_H 0.89 (9H, s, CH_3), 2.45 (1H, t, CH), 4.97-5.07 (4H, m, CH_2), 5.86 (2H, ddd, CH); δ_C 27.16 (CH_3), 32.74 (C), 59.56 (CH), 115.60 (CH_2), 138.57 (CH); *m/z* 124 (M^+,1), 109 (23), 91 (2), 81 (6), 68 (23), 67 (25), 57 (100), 55 (7).

A secondary product, 2-*tert*-butylbuta-1,3-diene, was also observed to form. δ_H 0.90 (9H, s, $C(\underline{C}H_3)_3$), 4.60 (1H, m), 4.85 (1H, dd, J = 16 Hz, 4 Hz), 4.88 (1H, m); 5.21 (1H, dd, J = 19 Hz, 4 Hz), 6.23 (1H, ddd, J = 19 Hz, 16 Hz). (Lit.[101]) δ_C 29.15 (CH_3), 34.85 ($\underline{C}(CH_3)_3$), 107.00 (CH_2), 114.87 (CH_2), 136.86 (CH), 156.60 (C). *m/z*. 110 (M^+, 32), 96 (59), 95 (100), 93 (19), 68 (24), 67 (42), 57 (57), 55 (36), 41 (57), 39 (26).

3-*tert*-Butylpenta-1,4-diene.

To a suspension of dichlorobis(triphenylphosphine)nickel (9.15 g; 14.0 mmol) and triphenylphosphine (7.34 g; 28.0 mmol) in dry degassed THF (40 cm^3), under N_2, was added 2.5 M *n*-butyl lithium (11.2 cm^3; 28.0 mmol in hexane). The solution went from dark green to brown. To this solution was added a mixture of 3-*tert*-butyl-1,5-dibromopentane (2.0 g; 7.0 mmol) and DBU (4.26 g; 28.0 mmol) in dry THF (20 cm^3) dropwise by syringe. The mixture was stirred at room temperature overnight, after which a metallic brown film was observed on the walls of the flask. The THF was distilled off in a Vigreux flask to leave a black viscous residue. Pentane was added and the solution became green. After stirring for 15 min. the solution was filtered and the pale green filtrate was distilled. After the pentane distilled over, the residue was distilled under reduced pressure to give a clear colourless liquid which was subsequently shown to be crude 3-*tert*-butylpenta-1,4-diene. The ^1H NMR and mass spectrum were as reported above.

3-*Iso*-propylpenta-1,4-diene

To a solution of penta-1,4-diene (1.0 g; 14.7 mmol) in dry THF (2.6 cm^3) at -78 °C under N_2 was added a solution containing 14.7 mmol of *n*-butyl lithium (9.2 cm^3 of a 1.6 M solution in hexane). The mixture was warmed to room temperature over 1 hr and was stirred for a further 2 hr. The lower, deep orange layer, which separated on standing, was removed by syringe and added dropwise to a solution of *iso*-propyl methanesulphonate (2.02 g; 14.6 mmol) in dry THF (2.6 cm^3) at -78 °C under N_2. The mixture was allowed to warm to room temperature, stirred overnight, briefly warmed to 50 °C, and then poured into 1 M NaOH (18 cm^3) and extracted with pentane (2 x 50 cm^3). The pentane extracts were washed (sat. $NaHCO_3$ aq., water), dried ($MgSO_4$ anhyd.), and distilled. The product distilled as a mixture with *n*-pentane and was purified by preparative GLC on a 20% Carbowax 20 M column (12') at 60 °C. (Lit.[102]) δ_H 0.87 (6H, d, CH_3), 1.66 (1H, m), 2.50 (1H, dd) 4.97-5.07 (4H, m, CH_2), 5.71-5.84 (2H, m, CH). δ_C 19.82 (CH_3), 31.70 (CH), 55.10 (CH), 114.88 (CH), 139.76 (CH_2), *m/z* 110 (M^+, 1), 95 (21), 68 (60), 67 (100), 54 (15), 43 (37), 41 (47), 39 (27).

Apart from 3-*iso*-propylpenta-1,4-diene, several $C_{11}H_{16}$ tetraenes were observed to form. Two of these tetraenes were isolated by preparative GLC (20% Carbowax 20 M; 12'; 120 °C) and identified as 3,5-divinylhepta-1,6-diene; δ_H 1.47 (2H, t, CH_2), 2.80 (2H, quintet, CH), 5.0 (8H, m, CH_2), 5.69 (4H, m, CH) δ_C 38.45 (CH), 44.93 (CH_2), 114.39 (CH), 140.86 (CH_2), *m/z* 147 (M-1, 1), 133 (5), 119 (8) 105 (12), 91 (15), 81 (31), 79 (80), 67 (100), 65 (27), 53 (31) and 3-vinylnona-1,6,8-triene δ_H 1.50 (2H, q), 2.10 (2H, q), 2.76 (1H, quintet), 5.03 (6H, m), 5.72 (3H, m) 6.05 (1H, m), 6.32 (1H, m), δ_C 12.28 (CH_2), 35.59 (CH_2), 43.74 (CH), 114.06 (CH_2), 116.42 (CH_2), 129.79 (CH), 133.60 (CH), 136.47 (CH), 140.32 (CH); *m/z* 148 (M^+,1), 133 (5), 119 (9), 106 (30), 91 (20), 81 (33), 79 (100), 67 (49), 53 (31).

Part Two

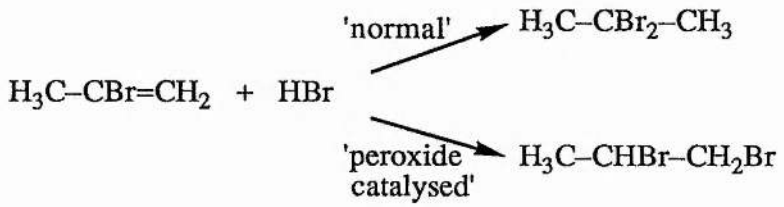
Sulphur Centred Free Radicals

Chapter Three

Introduction To Sulphonyl Radicals.

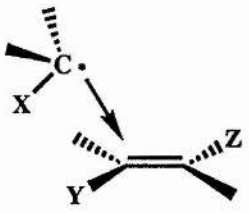
3.1 Free Radical Addition To Alkenes.

In 1937, Kharasch *et al.* reported the '*anti*-Markovnikov' addition of HBr to unsymmetrical alkenes under 'peroxide catalysed' conditions.[103]



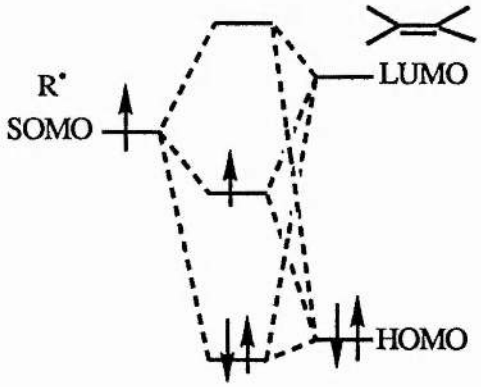
In a simultaneous review, Hey and Waters reported that the same reaction could be brought about by the action of ultraviolet light.[104] However, it was not until 1940, that Mayo and Walling offered any form of explanation to describe the orientation of such radical additions. They proposed that the polarity of the double bond had an insignificant effect on the point of attack by the bromine atom, but was determined by the relative stabilities of the two bromoalkyl radicals which may be formed.[105]

Additions of alkyl radicals to alkenes are strongly exothermic, since a σ bond is formed and a π bond is broken. Calculations favour an unsymmetrical transition state in which the distance between the attacking radical and the two vinylic carbons of the alkenes are unequal.



An unsymmetrical transition state readily explains the difference in the steric α and β effects. The distance between the β-alkene substituent Z and the radical is so large in the transition state that steric effects are insignificant. The α-substituent Y, is however, orientated towards the attacking radical and so is able to exert a repulsive force.

Free radical addition can be described in terms of frontier orbital theory. This states, approximately, that the energy difference between the HOMOs and LUMOs of the reacting species are decisive in determining rate variations. The smaller the energy difference between the frontier orbitals, the larger is the stabilising effect when the reactants approach one another. Thus, the interaction between the SOMO of a free radical and the LUMO and HOMO of the alkene should play an important role in the interpretation and prediction of polar effects.



Interaction between the SOMO and LUMO is decisive in reactions of alkyl radicals containing electron donating groups which increase the energy of the SOMO. The incorporation of electron withdrawing substituents into the alkene decreases the SOMO-LUMO energy difference and thus increases the rate of addition of the free radical. The nucleophilicity of alkyl radicals increases when electron donating substituents are incorporated into the radical since these also decrease the SOMO-LUMO energy difference. Thus, the *tert*-butyl radical reacts much more rapidly with electron deficient alkenes than does a primary or secondary radical. The SOMO-HOMO

energy difference is small for a *tert*-butyl radical so that variation of the substituent at the alkene exerts a large effect. In comparison, the SOMO-LUMO energy difference is larger for the primary hex-1-yl radical and hence the same variation of substituents at the alkene has less influence on the rate of addition. The *tert*-butyl radical is, therefore, not only more reactive, but also more selective than the primary hex-1-yl radical. Strong electron withdrawing substituents decrease the SOMO energy to such an extent that the SOMO-HOMO interaction becomes predominant. Radicals then lose their nucleophilic properties and become electrophilic.[106]

It can be clearly seen that free radical addition to alkenes is not a simple matter and that steric and polar effects, and bond strength are incorporated in determining the orientation of radical addition.

3.2 Sulphur Centred Radicals of Type $RSO_n^{\bullet}$.

3.2.1 Sulphinyl Radicals.

Sulphinyl radicals, $RSO^{\bullet}$, play an important part in organosulphur chemistry and biological systems. They have been formed by photolysis of sulphoxides ($RSOR'$)[107], sulphinyl chlorides ($RSOCl$)[108], organosulphites ($(R^1R^2CHO)_2S{=}O$)[109] and arene sulphinate esters ($ArSO.OR$).[110]

Synthetically sulphinyl radicals have not found much application, and thus information on their reactions is very limited. Early work indicated that sulphinyl radicals do not add to alkenes very readily.[111] However, more recent studies show that sulphinyl radicals add reversibly to styrene.[112]

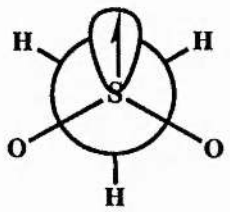
3.2.2 Sulphonyl Radicals.

Sulphonyl radicals, $RSO_2^{\bullet}$, are highly reactive transient species which are believed to occur in many chemical reactions, some of which are of great synthetic value. Sulphonyl radical reactions are also important in polymer chemistry, in air pollution and in some biological systems.

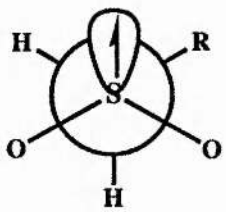
3.3 Nature of Sulphonyl Radicals.

For a sulphonyl radical $X–SO_2^{\bullet}$ it has been shown by examination of ^{33}S hyperfine splittings[113] in the solid state ESR spectrum that as the electronegativity of X increases, the radical becomes more pyramidal, corresponding to an increase in the *3s*-character on the sulphur and in turn to localisation of the unpaired electron on sulphur. Substituents which are electron donating reduce the total spin density on the sulphur atom and increase the percent occupancy of the *3p* orbital relative to the *3s* orbital indicating that the radical takes up a much flatter configuration.

The ESR spectrum of a large number of sulphonyl radicals have been obtained and the magnitudes of the hyperfine splittings have shown that the spin distribution in these species is typical of σ-radicals with a pyramidal centre at the sulphur, by analogy with the solid-state ESR data. The spin density is almost equally divided between sulphur and the two oxygens, the exact proportions depending upon the nature of X. The ESR spectrum of the methanesulphonyl radical indicates a staggered conformation, **1**, to be the most stable.[114] The replacement of an α-hydrogen by an alkyl group increases the activation energy for rotation about the C–S bond and the most stable conformation is close to rotamer **2**.

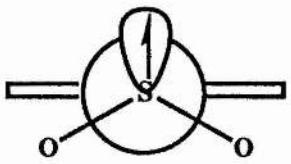


1



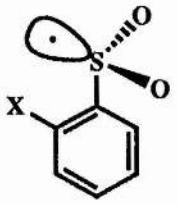
2

Arenesulphonyl radicals without *ortho*-substituents undergo relatively rapid rotation about the C–S bond, observable by ESR over a wide range of temperatures.[115] However, studies show that the benzenesulphonyl radical prefers to occupy a conformation, **3**, in which the singly occupied orbital is perpendicular to the aromatic ring.[116]



3

Some mono-*ortho*-substituted radicals, **4**, have been shown to occupy a conformation in which the unpaired electron mainly resides in a sulphur orbital in the plane of the ring, the sulphonyl oxygens lying *anti* to the *ortho*-substituent.

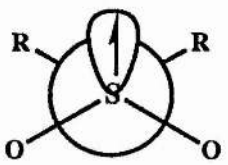


4

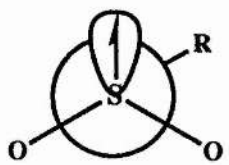
Di-*ortho*-substitution severely hinders C–S bond rotation so that it is slow at low temperatures.[115]

In the case of aminosulphonyl radicals, a small but significant π-spin density on nitrogen is obtained which is reflected in the similarity of the splittings from nitrogen, the α-protons (N–H), and the β-protons ($N–CH_3$) and that a formally conjugated structure, **5**, rather than a twisted conformation is preferred.[113]

The magnitude of the splittings in the alkoxysulphonyl radicals, which are dependent on temperature, indicates that alkoxysulphonyl radicals appear to prefer an asymmetrical conformation, as in **6**, to either of the two possible symmetrical conformations.[117]



5



6

3.4 Formation of Sulphonyl Radicals.

A great variety of methods have been used to generate sulphonyl radicals from several different types of precursor.

Use of dimethylsulphoxide with Ti(III)–H_2O_2 gives the methanesulphonyl radical *via* methanesulphinic acid. Hydrogen abstraction from the acid is carried out by methyl radicals which are also formed in the reaction.[118] Hydrogen abstraction from alkylsulphinic acids using *tert*-butoxyl radicals has been used and aromatic sulphonyl radicals have been generated from arylsulphinic acids by oxidation with ceric sulphate or direct photolysis.[116]

The usual method of sulphonyl radical generation for spectroscopic studies is halogen abstraction by triethylsilyl radicals from the corresponding sulphonyl chloride, **7**.

$$^tBuOOBu^t \longrightarrow 2\,^tBuO^\bullet$$

$$^tBuO^\bullet + Et_3SiH \longrightarrow {}^tBuOH + Et_3Si^\bullet$$

$$Et_3Si^\bullet + RSO_2Cl \longrightarrow Et_3SiCl + RSO_2^\bullet$$

7

Dissociative electron capture using sulphonyl chlorides has been used to generate sulphonyl radicals in pulse radiolysis experiments.[116]

$$RSO_2Cl + e^-_{aq} \longrightarrow [RSO_2Cl]^{\bullet-} \longrightarrow RSO_2^\bullet + Cl^-$$

Sulphonyl radicals are also formed when a radical reacts with sulphur dioxide

$$R^\bullet + SO_2 \longrightarrow RSO_2^\bullet$$

and several different radicals, R•, have been used to generate sulphonyl radicals in this manner.[118]

3.5 Radical Reactions of Sulphonyl Radicals.

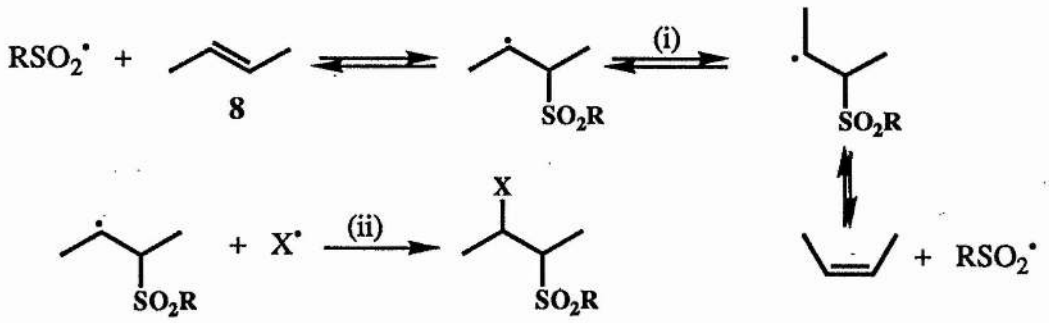
3.5.1 Abstraction.

The abstraction reaction is not a common feature of sulphonyl radical chemistry. Sulphinic acids have been observed in photochemical reactions of paraffin hydrocarbons and sulphur dioxide which probably result from hydrogen abstraction from alkanes by sulphonyl radicals.[119]

p-Toluenesulphonyl radicals, generated from *p*-toluenesulphonyl iodide, have been reported to abstract chlorine from carbon tetrachloride under certain conditions.[120]

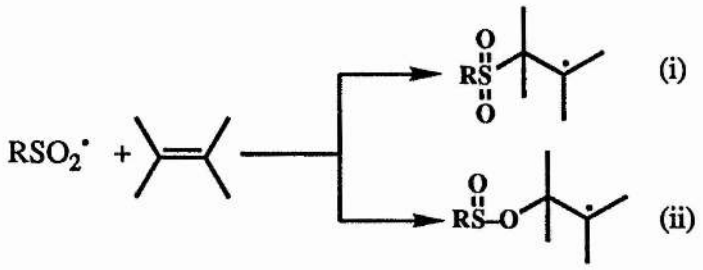
3.5.2 Addition.

Sulphonyl radical addition to alkenes has been shown to be a reversible reaction. In the case of but-2-ene, **8**, *cis-trans* isomerism of the alkene accompanies addition, *via* equilibrium (i);



which occurs much faster than adduct formation *via* reaction (ii).[121,122]

In principle, two possible pathways may exist for the addition of sulphonyl radicals to alkene double bonds, that is, attack by either the sulphur or an oxygen atom, because in sulphonyl radicals, the spin density is almost equally divided between sulphur and the two oxygens.



However, all preparative studies of reaction products have shown that reaction occurs exclusively through route (i).

3.6 Addition of Sulphonyl Halides to Alkenes.

The products of free radical addition of sulphonyl halides to alkenes are β-halosulphones, formed *via* a chain reaction in which $RSO_2^{\bullet}$ acts as a chain carrier.[123-131]

$$RSO_2X + In^{\bullet} \longrightarrow RSO_2^{\bullet} + InX$$

$$RSO_2^{\bullet} + R'CH{=}CH_2 \rightleftharpoons RSO_2CH_2\dot{C}HR'$$

$$RSO_2CH_2\dot{C}HR' + RSO_2X \longrightarrow RSO_2CHCHR' + RSO_2^{\bullet}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad X$$

Although sulphonyl chlorides add readily to unactivated alkenes, telomerisation and/or polymerisation occurs, but this may be suppressed by the use of catalytic amounts of copper (II) chloride (Asscher-Vofsi reaction)[121] or tris(triphenylphosphine) ruthenium (II) chloride, (Both of which are discussed in more detail in § 5.2).

The copper catalysed addition of sulphonyl chlorides to conjugated dienes, trienes,[132] aryl substituted cyclic alkenes,[133] and substituted styrenes[134] has been reported. Copper catalysis has also been used in sulphonyl iodide addition to simple and cyclic alkenes.[135]

Arene[136,137] and alkenesulphonyl chlorides[138] react with alkenes in the presence of tris(triphenylphosphine) ruthenium (II) chloride with 1 mol. equivalent of triethylamine to form α-β unsaturated sulphones in good yield.

The reaction of trifluoromethanesulphonyl chloride, **9**, with alkenes in the presence of tris(triphenylphosphine) ruthenium (II) chloride gives 1:1 adducts with extrusion of sulphur dioxide.[139]

$$\underset{\mathbf{9}}{CF_3SO_2Cl} + RCH{=}CH_2 \xrightarrow{RuCl_2(PPh_3)_3} RCHClCH_2CF_3 + SO_2$$

This is a useful method for the insertion of a trifluoromethyl substituent.

Ruthenium (II) chlorides have been used in free radical asymmetric addition of sulphonyl chlorides to alkenes.[140]

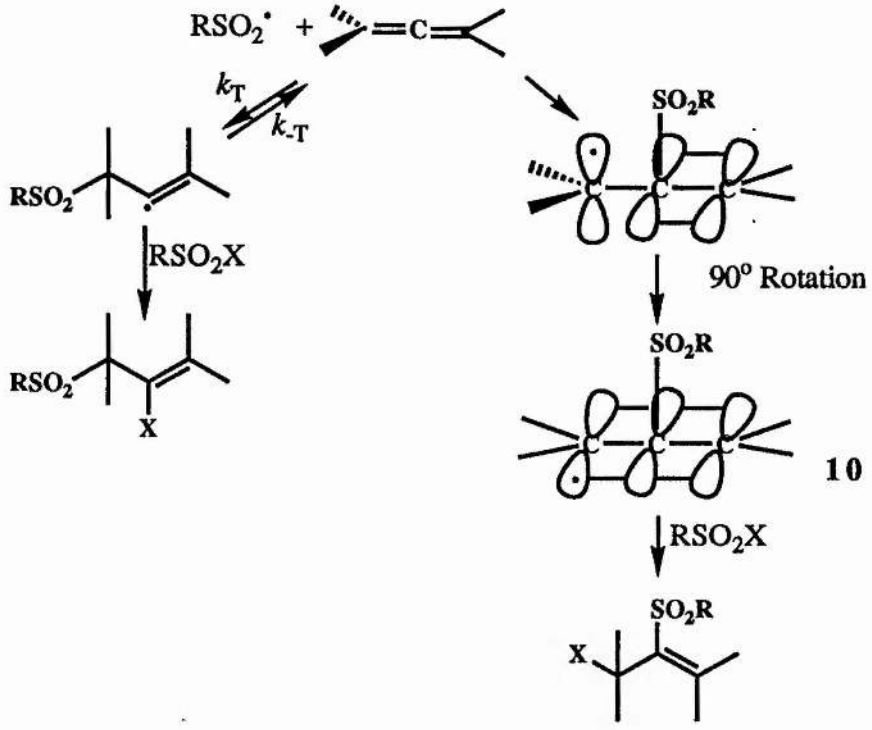
$$RSO_2Cl + Ph{-}CH{=}CHCH_3 \xrightarrow{Ru_2Cl_4(diop)_3} Ph{-}\overset{*}{C}H(Cl){-}CH(SO_2R)CH_3$$

Asymmetric synthesis is a growth area in synthetic organic chemistry and the above reaction is an efficient method of incorporating a chiral centre into a sulphonyl containing compound.

Addition of sulphonyl iodides to allenes such as phenylallene and 3-methyl-buta-1,2-diene has been found to give 1:1 adducts with regiospecific addition of the sulphonyl radical to the central position.[141] However, a mixture of products was observed on addition of sulphonyl iodides to propa-1,2-diene, due to attack at both central and terminal carbon atoms.

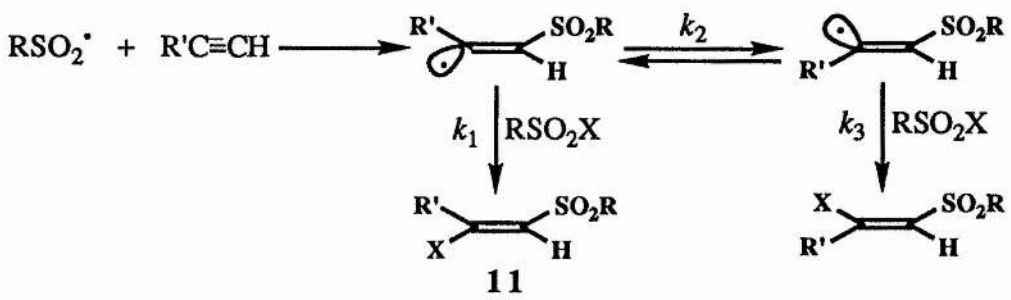
The preference for sulphonyl radicals to add to the central position of allenes is in contrast to the regiospecificity normally associated with free radical addition to allene. The proposed reason why this is observed is that because the π-bonds of allene are orthogonal, the rates of radical formation resulting either from central or terminal addition should be similar. However, the central carbon adduct formation is irreversible because the formed radical undergoes a rapid 90° rotation about the C–C axis to give a

resonance stabilised allyl radical, **10**.[141,142] This formation of a stabilised allyl radical is not not limited to sulphonyl radical addition and occurs for other radicals.[143]



Thus, the distribution of the final products will depend on the magnitude of the rate constants of the reversible reaction, k_T and the transfer reaction.

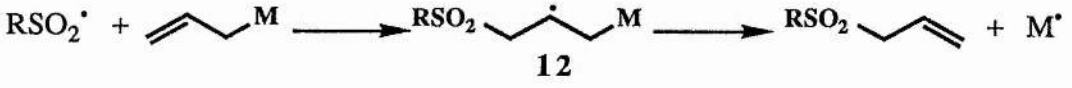
The addition of sulphonyl iodides[144] and bromides[145] to acetylenes has been observed, and 1:1 adducts form stereoselectively to give the *trans*-isomer. The predominance of the *trans*-isomer, **11**, may be because the chain transfer by sulphonyl halide (k_1) is much faster than isomerisation of the intermediate vinyl radical (k_2).



Copper-catalysed reaction of sulphonyl chlorides[146,147] or bromides[145] with acetylenes gives 1:1 adducts as mixtures of *trans*- and *cis*-β-halovinyl sulphones. Highly polar solvents favour *trans*-addition while solvents of low polarity favour *cis*-addition.[145,147]

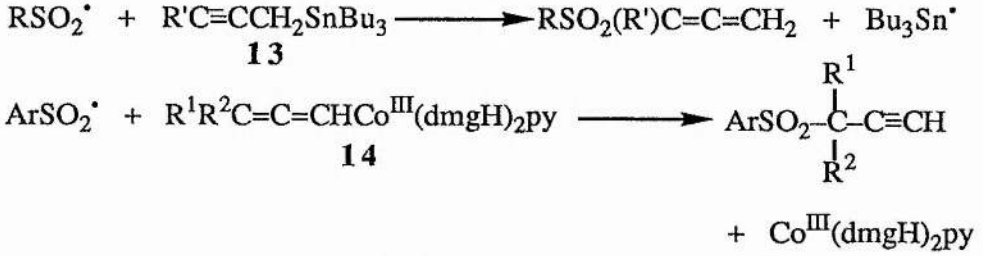
3.7 S_H2' Reactions.

Allyl, substituted allyl stannanes[148] and allyl cobaloximes[149] have been shown to undergo a S_H2' substitution *via* **12** to give sulphones.



12

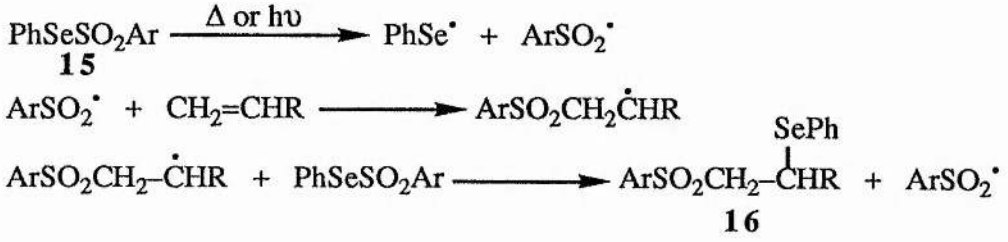
Similar types of substitution can be achieved with propargyl stannanes, **13**,[148] and allenyl cobaloximes, **14**.[150]



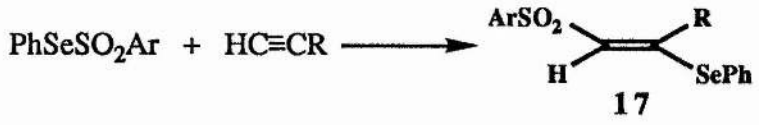
(dmgH) = monoanion of dimethylglyoxime

3.8 Selenosulphonylation of Alkenes.

Phenylareneselenosulphonates, **15**, undergo free radical addition to alkenes to give β-selenosulphones, **16**.[151,152] The addition occurs regiospecifically to give *anti*-Markovnikov products, and the following radical chain mechanism has been shown to operate.



When this addition is carried out with acetylenes it is both regiospecific and stereoselective to give the *E*-isomer of a β-(phenylseleno)vinylsulphone, **17**.[153]

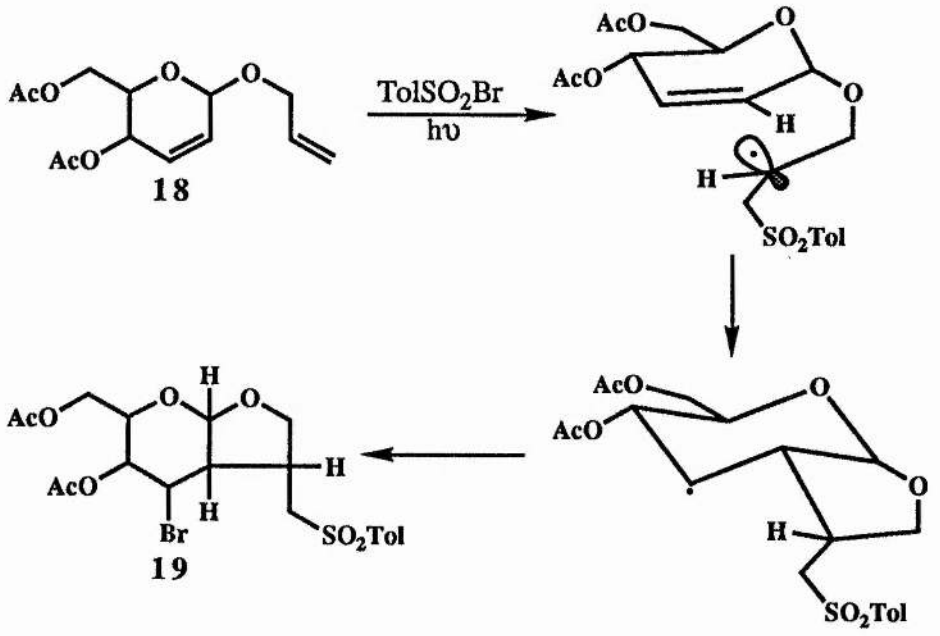


17

Selenosulphonylation of allenes has also been successfully carried out.[142]

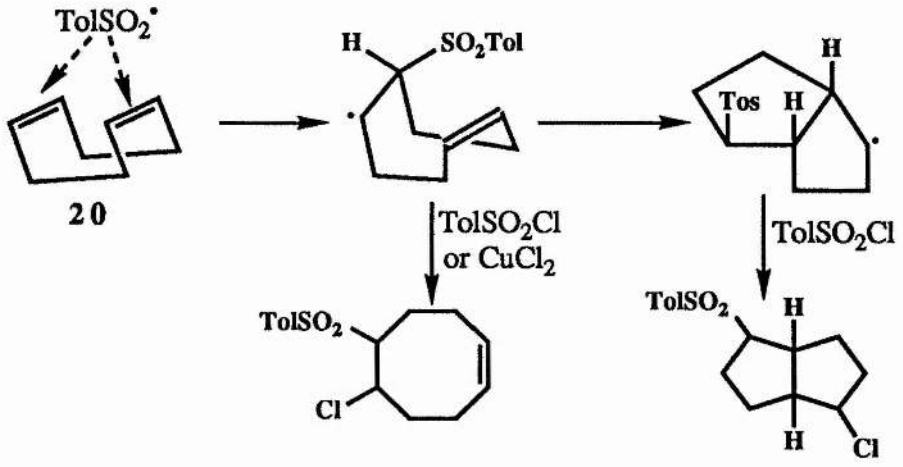
3.9 Sulphonyl Radicals in Carbon Centred Free Radical Cyclisation.

Sulphonyl radical addition to terminal alkenes has been used to promote free radical cyclisation. Note, that this is not cyclisation through the sulphonyl functionality itself, but through a radical centre β to the sulphonyl substituent. For example, addition of *p*-toluenesulphonyl bromide to a terminal alkene of an allyl glycal, **18**, has been shown to generate a pro-chiral carbon radical which adds to the glycal double bond with a high degree of diastereoselectivity to form a glycoside sugar unit, **19**.[154]



18 **19**

This type of sulphonyl addition-cyclisation reaction has been utilised in the cyclisation of 1,6-dienes, and cyclic dienes, including cycloocta-1,5-diene, **20**.[155]



3.10 Intramolecular Radical Cyclisation.

The intramolecular cyclisation of free radicals is a very important area of free radical chemistry. Increasing numbers of cyclisation reactions are being reported and many of them have been exploited as synthetically useful procedures.

3.10.1 Hex-5-enyl Radical Cyclisation.

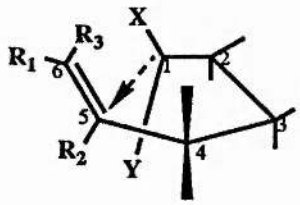
The problem of the cyclisation behaviour of the hex-5-enyl radical was first considered by Lamb *et al.*[156], examining the thermal decomposition of 6-heptenoyl peroxide in toluene at 77 °C. The hydrocarbon products obtained were found to be hex-1-ene (6%), methylcyclopentane (47%), cyclohexane (1%) and cyclohexene (trace). The hex-5-enyl radical was also observed to form by interaction of 6-mercaptohex-1-ene with triethylphosphite (to generate the hex-5-enyl radical *via* S_H2 reaction of the corresponding thiyl radical)[157] and Kolbe electrolysis of heptenoic acid,[158] both of which gave >95% 1,5 ring closure. The fact that methylcyclopentane was the major cyclised product was very puzzling since it would form from *anti*-Kharasch intramolecular addition of the hex-5-enyl radical, giving a primary rather than the secondary radical. As cyclohexane and methylcyclopentane were generated from diacyl peroxides at 77 °C in toluene it was concluded by Lamb that the intramolecular addition of the hex-5-enyl is irreversible and that the favoured formation of methylcyclopentyl

radical results from kinetic control. These results were later confirmed by Walling[159] and Kochi[160] at temperatures of 130 and 0 °C respectively.

3.11 Attempts To Rationalise The Selectivity Of Cyclisation.

3.11.1 Steric Hypothesis.

It has been suggested[161,162] that if the methylcyclopentyl and cyclohexyl radical transition states resemble the products, then it could be seen using models that in the case of the cyclohexyl transition state, **22**, there is a severe interaction between the C_2 and C_6 substituents. Since such an interaction is not present in the methylcyclopentyl transition state, **21**, the formation of the methylcyclopentyl radical would be favoured.



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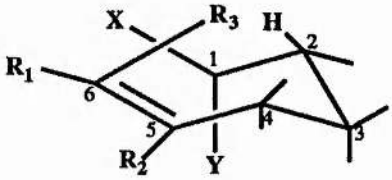
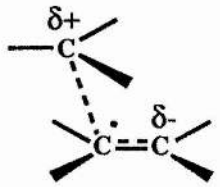


22

3.11.2 Stereoelectronic Hypothesis.

Another approach[163] is that cyclised products are formed *via* the thermodynamically less favoured route. Radical cyclisation, it was proposed, is largely under stereoelectronic control and that the transition state is sterically different from that which occurs in comparable cationic cyclisation reactions in which the 6-membered ring compound is usually formed.

It was suggested that the initial stages of the addition process involve interaction of the semi-occupied orbital (SOMO) with the lowest unoccupied orbital of the π-system (LUMO) and that the approach of the radical occurs along a line extending almost vertically from one of the terminal carbon atoms.



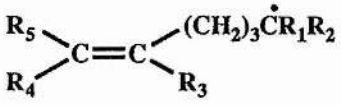
The basis for this model of the transition state rests on the suggestion that the primary interaction involves overlap of the half filled *2p*-orbital of the radical with one lobe of the vacant π^* orbital.[164] This helps explain why 1,5-cyclisation of the hex-5-enyl radical is preferred as the approach of the radical centre to C_5 is less constrained than in its approach to C_6.

If the radical centre of the hex-5-enyl radical is some atom (X) other than carbon the C_2–X bond length will vary according to the nature of X. Thus when the C_2–X bond length becomes shorter, the repulsive interaction of C_2–H/C_6–H increases and this disfavours cyclohexyl radical formation. It is expected that when X = CH_2, O or NR, the methylcyclopentyl radical will be favoured, but when X = S, there will be little if any preference between 5 or 6-membered ring formation.

A combination of both stereoelectronic and steric factors are best considered when dealing with this cyclisation.

3.12 Alkyl Substituted Hex-5-enyl Radicals.

It has been reported that alkyl substituents can markedly affect the intramolecular cyclisation of the hex-5-enyl radical.[165,166]

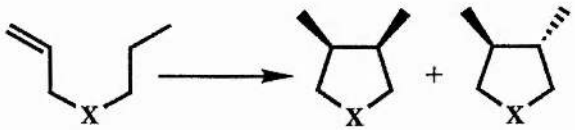


It has been shown that the nature of the initial radical, whether it is primary, secondary or tertiary (*i.e.* when R_1 and (or R_2) are H or alkyl) has little effect on the ratio of 1,5- to 1,6-cyclised products.

Alkyl substituents, R_4, in the *trans* 6-position also seem to have only a modest influence, although it can be expected from the Kharasch effect that the methylcyclopentyl radical is favoured and the cyclohexyl radical disfavoured. Thus, one can expect to observe a good yield of cyclised products with a high Cy_5/Cy_6 ratio with *trans*-alkyl substituents, R_4, than in the unsubstituted hex-5-enyl radical.

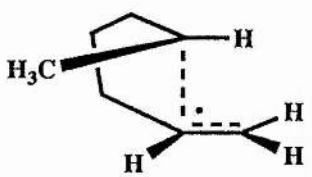
In the case of a substituent R_5 which is *cis* to the aliphatic chain, the Cy_5/Cy_6 ratio becomes so high that no six-membered ring species can be detected. Replacement of a *cis*-hydrogen, H–C_6, by a *cis*-alkyl group, R_5, will enhance the unfavourable interaction of R–C_6/H–C_2 in the cyclohexyl radical transition state. The *cis*-alkyl R_5 group increases the Cy_5/Cy_6 ratio by decreasing $k_{1,6}$ rather than by increasing $k_{1,5}$ and as expected a decrease in the total yield of cyclised products is observed.

Hex-5-enyl radicals bearing a substituent at C_1 give a mixture of *cis*- and *trans*-disubstituted compounds by 1,5 ring closure. Preferential formation of the latter would be expected since the transition state for *trans*-cyclisation is less subject to non-bonded interactions than for *cis*-cyclisation. However, both the hept-6-en-2-yl radical and the allyloxyprop-2-yl radical afford mainly the *cis*-products, **23**.



X = CH_2, O **23**

This has been attributed[167] to the favourable interaction, in the transition state for *cis*-cyclisation, between the hyperconjugatively delocalised orbital of the attacking radical and the π^* orbital of matching symmetry.[168]



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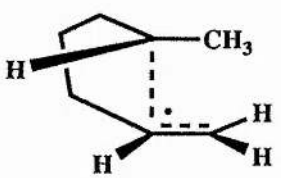

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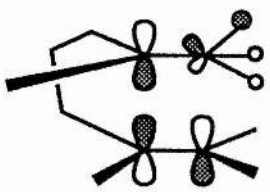

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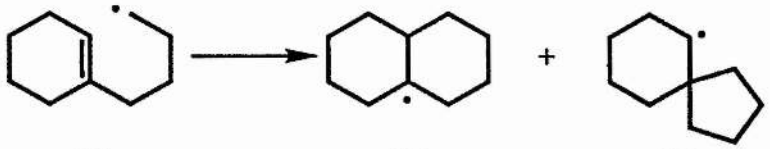
On thermodynamic grounds *trans*-cyclisation would be expected to be more favourable than *cis*- since the transition state for the former process is less prone to non-bonded repulsive interactions than that of the latter. However, application of orbital symmetry considerations results in a contrasting view. One model for the transition state for alkyl radical addition to a double bond involves interaction of the half-filled *p*-orbital with the vacant π^* orbital. Hyperconjugative mixing of the former with adjacent CH σ and σ^* orbitals produces a modified delocalised orbital which is of similar symmetry to the acceptor π^* orbital. Thus in transition state **25** leading to the *cis*-disubstituted product there is a secondary attractive interaction between the alkyl substituent and the double bond (**26**) which is not available in transition state **24** for *trans*-cyclisation.

The secondary interaction is important only in the region of distant approach. As the C–C separation diminishes, the rapidly rising closed shell repulsions of interacting occupied CH_3 levels takes over and destabilises the eclipsed approach.

It can be concluded, therefore, that in highly exothermic association reactions where the transition state occurs at large separation of reaction partners, the activation energy for the path leading to the sterically more hindered product may be lower.

3.13 Bicyclic And Polycyclic Rings.

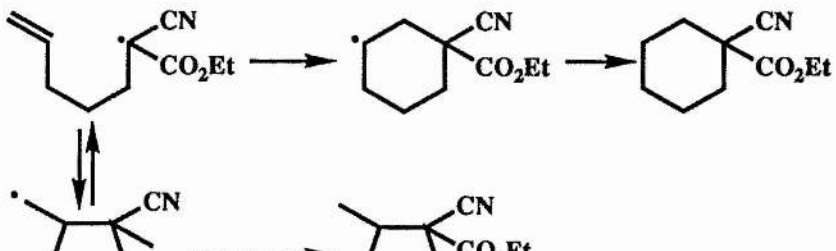
It is possible to synthesise bicyclic and polycyclic compounds by intramolecular radical cyclisation. Ring closure of the cyclohexenylbutyl radical, **27**,[163,169,170] affords the 9-decalyl, **28**, and spirodecyl radicals, **29**. Formation of the spirodecyl radical[169] is slightly favoured ($k_{1,5}/k_{1,6}$) but both modes of cyclisation are considerably slower than that of the hex-5-enyl radical.[171] In this case the relative yields of *cis*- and *trans*-decalin formed depend upon the nature of the hydrogen donor, (*cis*/*trans* = 0.17 for Bu_3SnH).



27 28 29

3.14 Stabilising Groups On The Carbon Radical Centre.

It has been discussed how in the hex-5-enyl radical, $CH_2=CH(CH)_2C^{\bullet}XY$, where X and Y are alkyl groups, they have little effect on the yields and ratios of the cyclised products. However, when X and Y are groups which can stabilise a carbon centred free radical, different results are obtained. In some cases only the 6-membered ring product is obtained. These types of cyclisation often proceed to give excellent yields of products in synthetically useful reactions. Formation of the initial radical is also very easy, probably due to the stabilised nature of the radical. Refluxing $CH_2=CH(CH_2)_3CH(CN)(CO_2Et)$ in cyclohexane at 80 °C (di-*tert*-butyl peroxide as initiator) gives products of which the *Cy*5 /*Cy*6 ratio is 16:84 in 58% yield.[172,173]

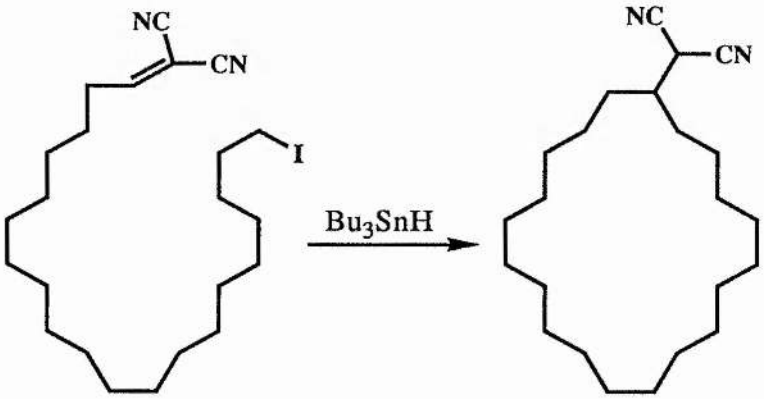


3.15 Higher Homologues.

In contrast to the hex-5-enyl radical, $CH_2=CH(CH_2)_nCH_2^{\bullet}$; (n=3), the other homologues have not been extensively studied. When n=4 or more, cyclisation occurs with relative difficulty, and is often so slow as to render the reaction unsuitable for synthetic purposes. Formation of methylcycloalkanes is again favoured with the higher homologues.[174] However, the *Cy*5/*Cy*6 selectivity which is about 50, is only 6 in the *Cy*6/*Cy*7 case. Stereoelectronic constraints on the regioselectivity of ring closure

become less severe with increasing chain length. Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are more favourable towards formation of the smaller ring.

Despite this apparent difficulty in the cyclisation of larger radical chains, recent work by Porter has revealed that free radical macrocyclisation can be used to prepare large rings, providing the steric and polar effects of the precursors are taken into account. Yields of up to 75-80% have been achieved with chain lengths of up to 15 carbon atoms.[175] The method has been developed as a suitable synthesis of lactones of ring sizes in excess of 11 atoms.[176] An example of a free radical macrocyclisation reaction is the intramolecular cyclisation of 1,1-dicyano-21-iodo-1-heneicosane, **30**, to give (dicyano-methyl)cycloeicosane, **31**, in 53% yield.[177]



30 **31**

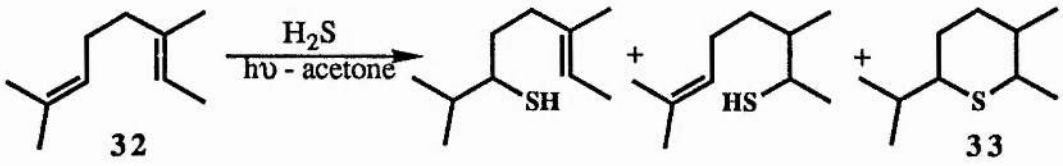
3.16 Lower Homologues.

If the model proposed by Beckwith (which involves the necessity for the radical to be above the plane of the double bond) is accepted, it is clear that this will become more difficult as the chain length shortens. In fact, cyclised products have not been observed with the pent-4-enyl and but-3-enyl radicals when they are generated from the corresponding bromides. Although 1,4 ring closure of the pent-4-enyl radical to give the methylcyclobutyl radical meets the stereoelectronic requirements for intramolecular addition, it is disfavoured on thermodynamic grounds. Because of ring strain the cyclisation is endothermic, and the equilibrium must lie well to the left.

3.17 Sulphur Centred Radicals.

As noted above the cyclisation of alkoxy and aminyl radicals mirrors that of the carbon centred hex-5-enyl radical under kinetic control, but the sulphur centred radical has roughly equal preference for 1,5 or 1,6 cyclisation.

Cyclisation of unsaturated mercaptans was first described in 1947 by Naylor,[178] who photolysed hydrogen sulphide with 2,6-dimethylocta-2,6-diene, **32**. Since under ionic conditions other products are obtained, it can be assumed that the thiapyran, **33**, obtained results from intramolecular addition of the corresponding thiyl radical.



32 **33**

Also of importance are the results of Dyer and Osborne[179] who, by distillation of 6-mercaptohex-1-ene obtained a mixture of tetrahydro-2-methylthiapyran (*Cy*6) and thiepan (*Cy*7). However, it was not until 1964 that Walling proposed that 2-methyl-tetrahydrothiophene (*Cy*5) and thiacyclohexane (*Cy*6) obtained as contaminants in the preparation of 5-mercaptopent-1-ene were formed by intramolecular addition of the thiyl radical to the double bond.[157]

If conditions are chosen to minimise the competitive polymerisation reaction, *i.e.* under high-dilution conditions, intramolecular addition of unsaturated thiyl radicals, generated by peroxide initiation or by photolysis of the corresponding unsaturated mercaptans, appears to occur more easily than with other radicals discussed previously. For instance, not only in the *Cy*5/*Cy*6 but also in the *Cy*4/*Cy*5, *Cy*6/*Cy*7 and even the *Cy*7/*Cy*8 case, yields of up to 90% of cyclised products may be obtained. It appears that the main reason which has been proposed to explain both the ease of cyclisation and the lack of selectivity is the large bond length of the C–S$^{\bullet}$ compared to C–C$^{\bullet}$, C–O$^{\bullet}$ and C–N$^{\bullet}$. The orthogonal overlap of the thiyl radical with the double bond will be

easier but this time at either end since the unfavourable steric interactions which hinder addition to the terminal position of the double bond will be decreased.

A feature which often drastically alters the ratio of the two cyclised products is the reversibility of the intramolecular addition of thiyl radicals. It is clear, therefore, that forecasting or even interpreting the results of intramolecular addition of thiyl radicals is not a simple matter, the major product is often not the one expected from the best known behaviour of carbon radicals. Thus, the influence of substituents may make any comparisons even more difficult to understand. Addition of thiyl radicals to alkenes is reversible[180] and so ring closure of such radicals lacks regiospecificity, for example, pent-4-ene- and hex-5-ene-1-thiol (n = 2 and 3 respectively) afford mixtures of *exo*- and *endo*-cyclised products when heated in cyclohexane.[181]

n	Relative Yield%	
2	24	76
3	85	15

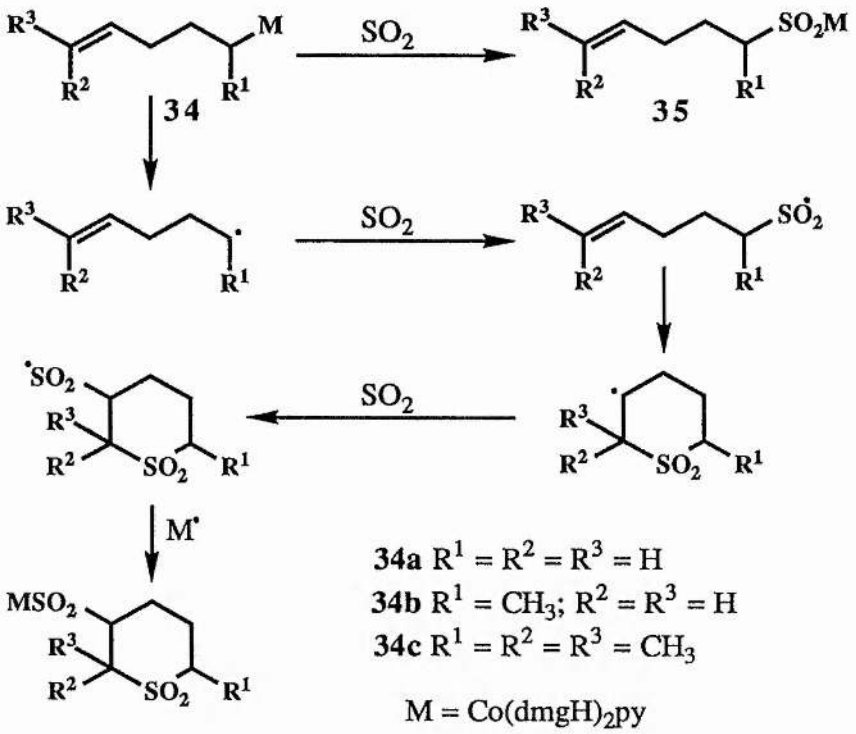
There is an increasing preference shown for *endo*-cyclisation with increasing reaction temperature or decreasing thiol concentration. Although various explanations are possible, the most straight forward is that $k_{exo} > k_{endo}$. If so, this implies that ring closure of thiyl radicals, like those of N- C- and O-centred radicals is subject to stereoelectronic control.

3.18 Cyclisation of Sulphonyl Radicals.

In view of the potential of intramolecular cyclisation of sulphonyl radicals to prepare cyclic sulphones, it is surprising that almost nothing has been reported in this area.

Johnson and Derenne showed that 6-methylhept-5-en-2-ylcobaloxime (III) reacts with sulphur dioxide to give 1,1-dioxathiacyclohexane-3-sulphonyl cobaloxime,

in which two molecules of sulphur dioxide have been inserted. The product is believed to form through homolysis of the C–Co bond, reaction with sulphur dioxide to give a sulphonyl radical and then cyclisation.



34a $R^1 = R^2 = R^3 = H$
34b $R^1 = CH_3$; $R^2 = R^3 = H$
34c $R^1 = R^2 = R^3 = CH_3$

$M = Co(dmgH)_2py$

In the case of pent-4-enylcobaloxime, **34a**, in the reaction with sulphur dioxide, the major product is the insertion product, **35**. However, the secondary alkenyl analogues, **34b** and **34c** give lower yields of the normal insertion product and high yields of organocobaloximes containing two SO_2 moieties, formed through a sulphonyl radical cyclisation step.[182]

A similar reaction has been observed in the reaction between trichloromethanesulphonyl chloride and pent-4-enylcobaloximes.[183] Here, termination of the cyclisation may occur by abstraction of chlorine from the sulphonyl chloride to give chlorinated cyclic sulphones.

Chapter Four

Sulphonate Esters As Radical Precursors.

4.1 Sulphonyl Radicals From Sulphonate Esters.

In order to generate a free radical it is necessary to prepare a precursor with a substituent which can be selectively removed from a specific position to form the desired radical. One of the commonest groups of radical precursors are the alkyl bromides, which upon selective debromination with organotin or organosilyl radicals give the corresponding alkyl radical. Bromides are often prepared from the alcohol *via* the methanesulphonate ester. As bromides are often unstable or difficult to handle it was decided to investigate whether the intermediate sulphonate esters would be suitable as radical precursors.

Sulphonate esters, **1**, were readily prepared from an alcohol and a sulphonyl chloride in the presence of base, usually in good yield.

$$RSO_2Cl + R'OH \xrightarrow{Et_3N} \underset{\mathbf{1}}{RSO_2OR'}$$

Mixtures of the sulphonate ester, hexamethylditin (or triethylsilane) and di-*tert*-butyl peroxide in *tert*-butylbenzene were photolysed in the cavity of an ESR spectrometer. In most cases the spectrum of the corresponding sulphonyl radical, $RSO_2^{\bullet}$, was observed rather than that of the alkyl radical, $R^{\bullet}$, (*e.g.* $CH_3SO_2^{\bullet}$, Figure 3). It is probable that these sulphonyl radicals are formed when the trimethyltin or triethylsilyl radicals undergo an S_H2 reaction with the sulphonate ester.

$$RSO_2OR' \xrightarrow{R_3X^{\bullet}} RSO_2^{\bullet} + R'OXR_3$$

X = Sn, Si

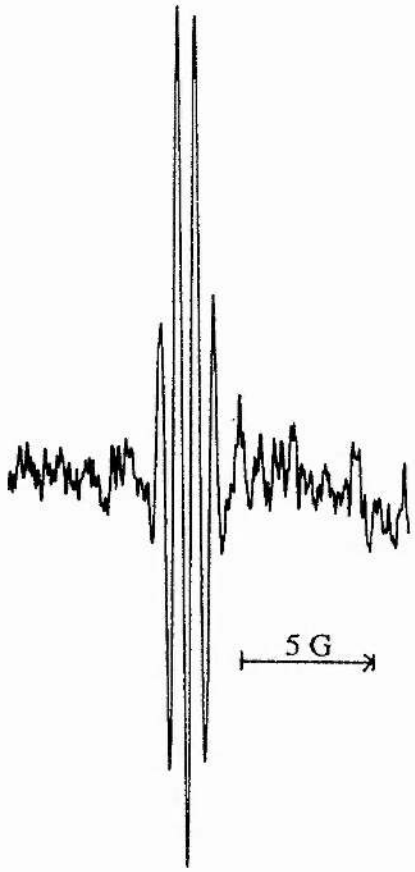


Figure 3. ESR Spectrum Of The Methanesulphonyl Radical.

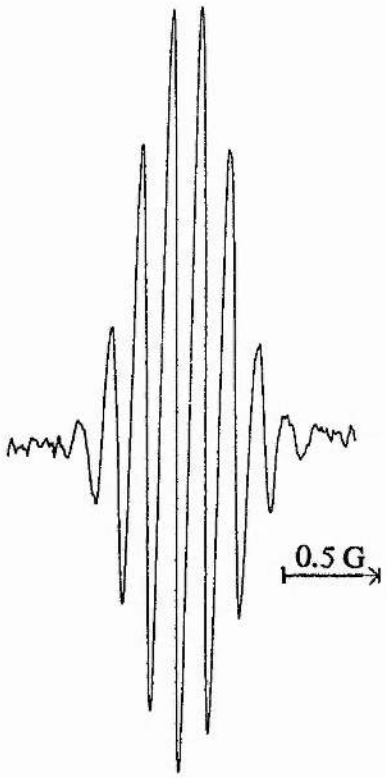


Figure 4. ESR Spectrum Of The *tert*-Butoxysulphonyl Radical.

ESR Parameters For Sulphonyl Radicals.

Radical	T/K	Observed	Literature g-value	Literature h.f.s
$CH_3SO_2^{\bullet}$	240	*a*(3H) 0.7	2.0049	*a*(3H) 0.7 [114]
i-$PrSO_2^{\bullet}$	240	*a*(6H) 2.1	2.0052	*a*(1H) 0.4, *a*(6H) 1.9 [114]
p-$CH_3C_6H_4SO_2^{\bullet}$	240	*a*(*m*-H) 1.20, *a*(*o*-H) 0.34 *a*(3H) 0.70	2.0045	*a*(*m*-H) 1.18, *a*(*o*-H) 0.32, *a*(3H) 0.65 [107]
$CF_3SO_2^{\bullet}$	240	not observed[a]	2.0052	*a*(3F) 15.5 [110]
$Me_3SiCH_2SO_2^{\bullet}$	240	*a*(9H) 0.64, *a*(2H) 3.4		

a- $CF_3SO_2^{\bullet}$ α-scission product identified (see § 4.2).

This reaction was carried out on a preparative scale using tri-*n*-butyltin hydride as the radical source and UV light as the initiator. Under these conditions, *iso*-propyl *p*-toluenesulphonate, **2**, gave *p*-toluenesulphinic acid, **3**, which forms when the *p*-toluenesulphonyl radical abstracts hydrogen from the tin hydride.

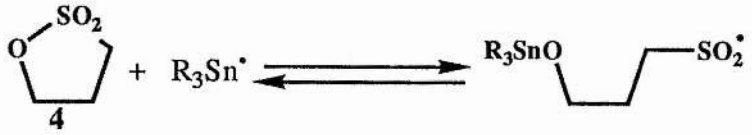
$$\underset{\mathbf{2}}{\text{p-}CH_3C_6H_4SO_2OCH(CH_3)_2} \xrightarrow{Bu_3Sn^{\bullet}} \text{p-}CH_3C_6H_4SO_2^{\bullet} \xrightarrow{Bu_3SnH} \underset{\mathbf{3}}{\text{p-}CH_3C_6H_4SO_2H}$$

Sulphonate esters, RSO_2OR' (see Table 1) always gave the corresponding sulphonyl radical (except where a secondary radical is formed in cases where R' is a terminally unsaturated substituent- see § 4.3), and this was observed for R = CH_3, $CH(CH_3)_2$, and CCl_3. However, weak spectra or no radicals at all were observed when R = *p*-$CH_3C_6H_4$, probably due to the aryl group absorbing too much UV light. No radicals were observed when R = CF_3, which may be attributable to difficulties in observing the trifluoromethanesulphonyl radical (see § 4.2).

Table 1

R	R'	Radical Observed
CH_3	*n*-C_6H_{13}	$CH_3SO_2^{\bullet}$
CH_3	CH_2Ph	$CH_3SO_2^{\bullet}$
CH_3	*c*-C_5H_9	$CH_3SO_2^{\bullet}$
CH_3	*p*-$CH_3OC_6H_4$	$CH_3SO_2^{\bullet}$
CH_3	$CH_2C(O)CH_3$	$CH_3SO_2^{\bullet}$
CH_3	$C(CH_3)_2C(O)CH_2CH_3$	$CH_3SO_2^{\bullet}$
CH_3	$C(CH_3)_3$	$CH_3SO_2^{\bullet}$
CH_3	2-cyclohexenyl	$CH_3SO_2^{\bullet}$
CH_3	$CH(CH_3)_2$	$CH_3SO_2^{\bullet}$
CH_3	$CH_2CH=CH_2$	$CH_3SO_2^{\bullet}$
CH_3	$CH(C=C(CH_3)_2)_2$	$CH_3SO_2^{\bullet}$
p-$CH_3C_6H_4$	*n*-C_6H_{13}	No Signal
p-$CH_3C_6H_4$	$CH_2CH=CH_2$	*p*-$CH_3C_6H_4SO_2^{\bullet}$
CF_3	*n*-C_6H_{13}	No Signal
CCl_3	CH_2Ph	$CCl_3SO_2^{\bullet}$
CCl_3	$CH_2CH=CH_2$	$CCl_3SO_2^{\bullet}$
CCl_3	$C(CH_3)_3$	$CCl_3SO_2^{\bullet}$
$(CH_3)_2CH$	CH_2Ph	$(CH_3)_2CHSO_2^{\bullet}$
$(CH_3)_2CH$	$CH_2C(O)CH_3$	$(CH_3)_2CHSO_2^{\bullet}$
$(CH_3)_2CH$	$C(CH_3)_3$	$(CH_3)_2CHSO_2^{\bullet}$

Whilst sulphonyl radicals were readily observed with a variety of sulphonate esters, it was found that sultones such as 1,3-propane sultone, **4**, (effectively cyclic sulphonate esters) did not produce radicals observable by ESR. This may be because once the sulphonyl radical forms, it cyclises back to the sultone before the steady state concentration increases to a level observable by ESR, or because of the poor solubility of the sultone in hydrocarbon solvents.



4.2 Sulphonyl Radicals.

Sulphonyl radicals may undergo α-scission to give sulphur dioxide and a new radical.[116]

$$RSO_2^{\bullet} \longrightarrow R^{\bullet} + SO_2$$

This was occasionally observed with some of the sulphonyl radicals generated in this work. α-Scission was not observed with methane- or toluenesulphonyl radicals which are presumably fairly stable over the accessible temperature range, however, trihalogenated methanesulphonyl radicals were found to readily undergo α-scission. The trichloromethanesulphonyl radical (observed as a singlet, with a *g*-value typical of other sulphonyl radicals) was found to undergo α-scission which was observed by a slow build up of the trichloromethyl radical, **5**; $a(^{35}Cl)$ 6.3, $a(^{37}Cl)$ 5.5; Lit.[184,185] $a(3^{35}Cl)$ 6.25, $a(^{37}Cl)$ 5.20 .

$$CCl_3SO_2^{\bullet} \longrightarrow CCl_3^{\bullet} + SO_2$$
5

With the trifluoromethanesulphonyl radical, generated from the corresponding sulphonyl chloride, the parent sulphonyl radical was never observed (though it has been reported previously),[110] even over a wide temperature range (162-280 K). The trifluoromethyl radical also remained undetected, though α-scission was probably occurring because the *tert*-butoxysulphonyl radical, **6**, (Figure 4) was observed, *a*(9H) 0.27; Lit.[186] *a*(9H) 0.28. This forms when SO_2, formed through α-scission, reacts with the *tert*-butoxyl radical.

$$^tBuOOBu^t \xrightarrow{h\upsilon} 2\ ^tBuO^{\bullet}$$
$$^tBuO^{\bullet} + Me_3SnSnMe_3 \longrightarrow Me_3Sn^{\bullet} + Me_3SnOBu^t$$
$$CF_3SO_2Cl + Me_3Sn^{\bullet} \longrightarrow CF_3SO_2^{\bullet} + Me_3SnCl$$
$$CF_3SO_2^{\bullet} \longrightarrow CF_3^{\bullet} + SO_2$$
$$^tBuO^{\bullet} + SO_2 \longrightarrow {}^tBuOSO_2^{\bullet}$$
6

That the observed radical was attributable to *tert*-butoxyl radical addition rather than trimethyltin radical addition to SO_2 was confirmed by photolysis of separate solutions of di-*tert*-butyl peroxide and hexamethylditin in pentane, through which SO_2 had been bubbled.

$$^tBuO^{\bullet} + SO_2 \longrightarrow {}^tBuOSO_2^{\bullet}$$

$$Me_3Sn^{\bullet} + SO_2 \longrightarrow Me_3SnSO_2^{\bullet}$$

Comparison of the h.f.s of the adduct radicals and those reported in the literature for the *tert*-butoxysulphonyl radical[186] confirmed the proposed scheme.

Trimethylsilylmethanesulphonyl chloride, **7**, was prepared from the isothiouronium salt which in turn was prepared from chloromethyltrimethylsilane and thiourea.[187,188]

$$Me_3SiCH_2Cl + (NH_2)_2C{=}S \longrightarrow Me_3SiCH_2\text{-}S\text{-}C(NH_2){=}\overset{+}{N}H_2\ \overset{-}{Cl}$$

$$\xrightarrow{H_2O/Cl_2} Me_3SiCH_2SO_2Cl$$

7

The trimethylsilylmethanesulphonyl radical, (a(2H) 3.4, a(9H) 0.64), was generated from the sulphonyl chloride using photochemically generated trimethyltin radicals.

$$Me_3SiCH_2SO_2Cl \xrightarrow{Me_3Sn^{\bullet}} Me_3SiCH_2SO_2^{\bullet} \xrightarrow{X} Me_3SiSO_2CH_2^{\bullet}$$

It has been observed previously that in certain radicals, the silyl group can migrate from carbon to oxygen[189], sulphur[190] or nitrogen[191] and the nature of the trimethylsilylmethanesulphonyl radical (Figure 5) suggested a similar migration from carbon to sulphur may occur. The radical was observed over a wide temperature range (160-320 K) but none of the rearranged radical, $Me_3SiSO_2CH_2^{\bullet}$, was detected by ESR spectroscopy.

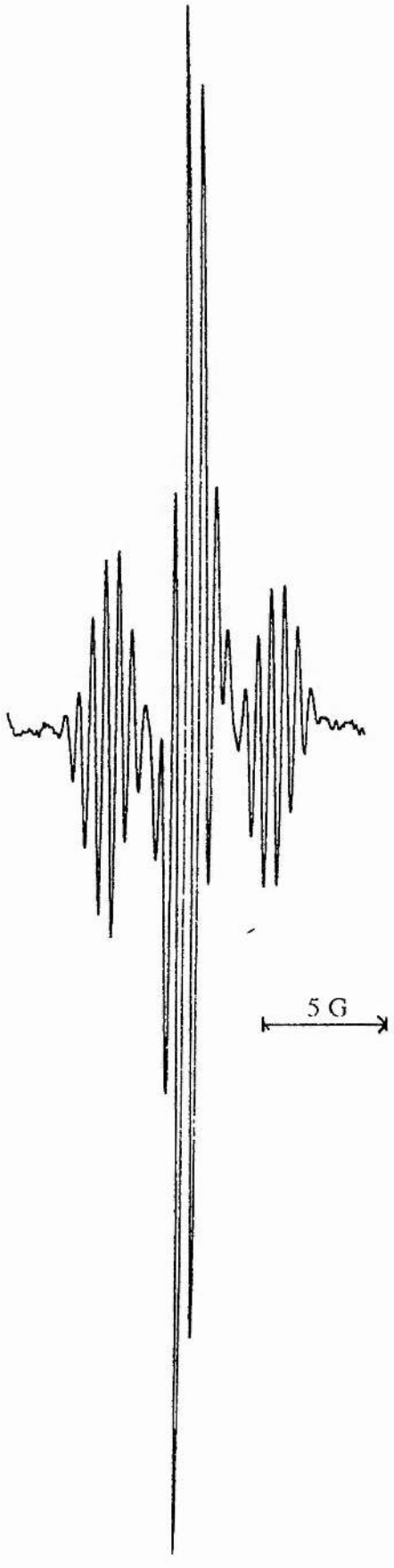


Figure 5. ESR Spectrum Of The Trimethylsilylmethanesulphonyl Radical.

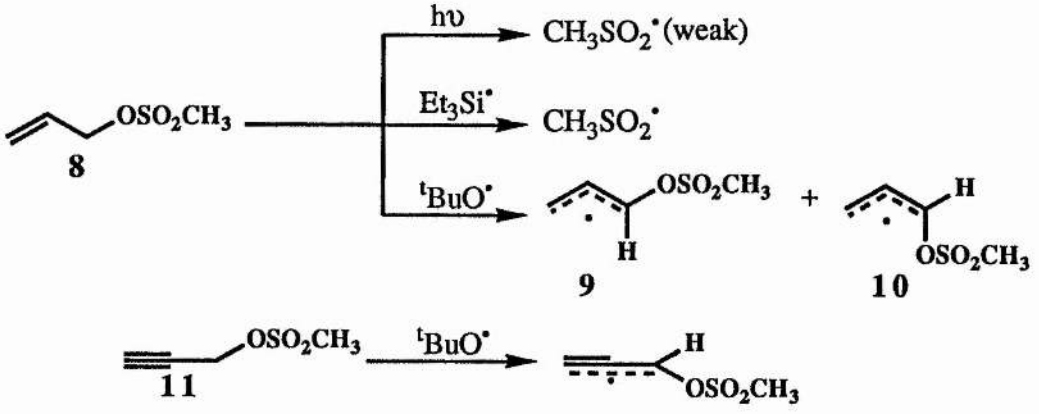
4.3 Radical Generation From Unsaturated Sulphonate Esters.

Certain alkenyl- and alkynylsulphonate esters behave differently under free radical conditions from their alkyl and aryl counterparts by virtue of their unsaturated moiety. With allyl methanesulphonate it was possible to demonstrate that under differing conditions, several different reaction pathways occur.

Photolysis of allyl methanesulphonate, **8**, results in the cleavage of the S–alkoxy bond to give the methanesulphonyl radical, but this process was inefficient and the concentration of the sulphonyl radical produced was very low, as shown by the ESR spectra.

The intensity of the signal could be substantially improved by the reaction of allyl methanesulphonate with photochemically generated triethylsilyl radicals. The triethylsilyl radical displaces the methanesulphonyl radical which was observed in high concentration. The above reactions apply equally to the alkyl and arylsulphonate esters previously discussed, however, the reaction of unsaturated esters with other radicals often differs.

Hydrogen abstraction is the preferred mode of reaction with photochemically generated *tert*-butoxyl radicals to give the *syn*- and *anti*- substituted allyl radicals, **9** and **10**, (Figure 6) with some sulphonyl radical also being observed. A substituted propynyl radical was observed in an analogous reaction using propynyl methanesulphonate, **11**. Hydrogen abstraction by *tert*-butoxyl radicals is not unexpected, especially as the product radical is stabilised by delocalisation.



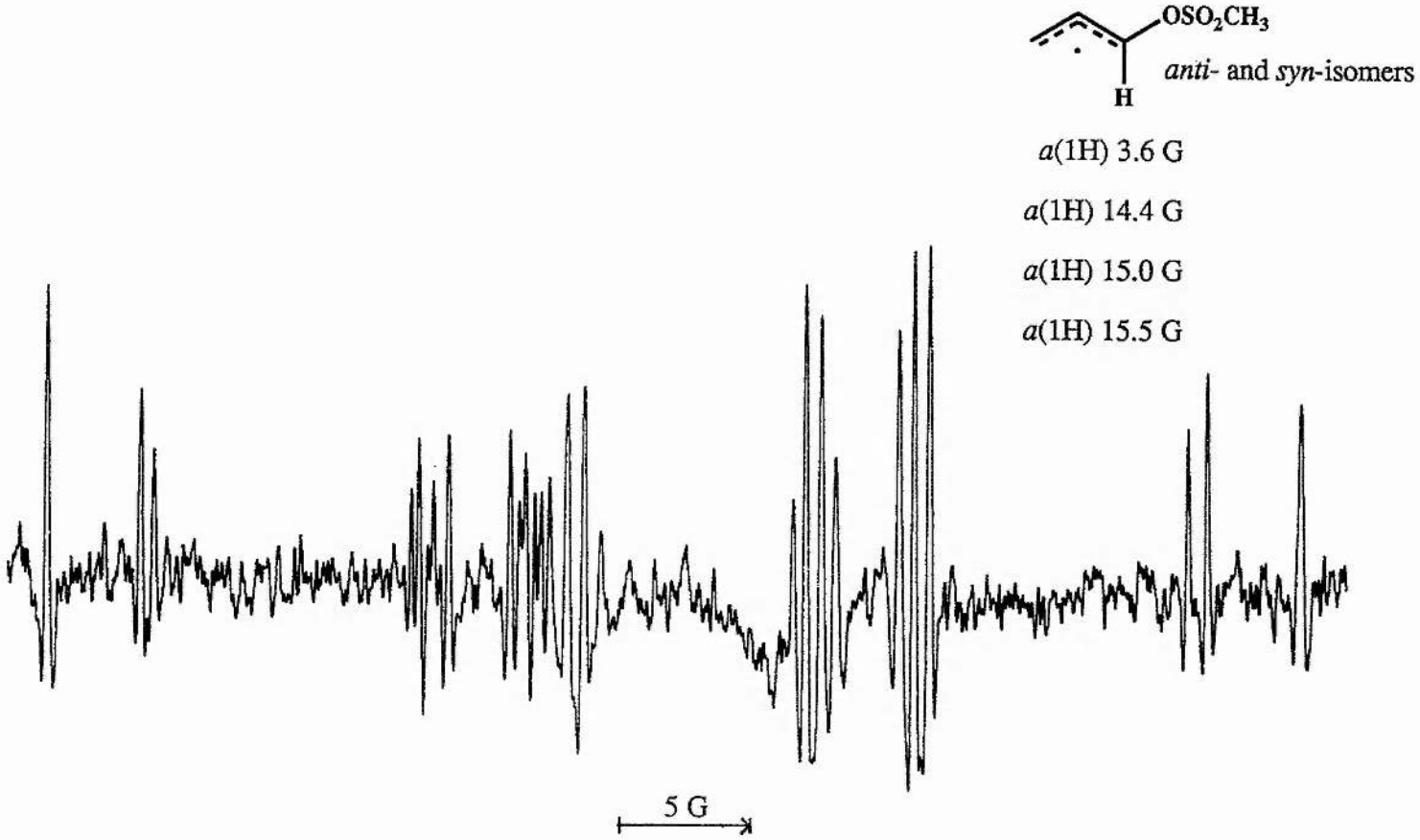
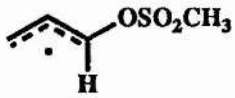
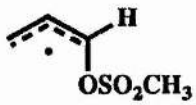
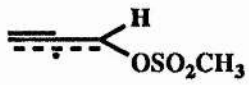


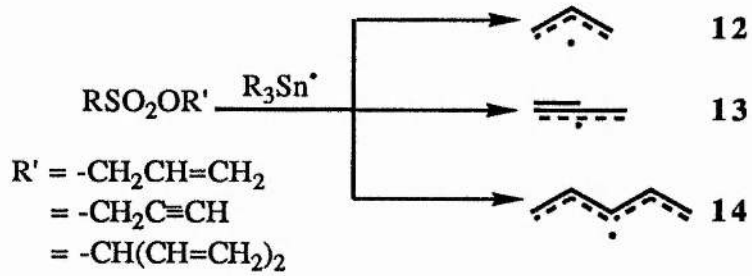
Figure 6. ESR Spectrum Of The MethaneSulphonate Substituted Allyl Radical.

The h.f.s for the observed substituted allyl radicals are shown in Table 2 below;

Table 2

Radical	g-value	h.f.s/G
	2.0026	*a*(1H) 3.6, *a*(1H) 14.4, *a*(1H) 15.0, *a*(1H) 15.5
	2.0026	*a*(1H) 4.4, *a*(1H) 14.0, *a*(1H) 14.7, *a*(1H) 15.2
		*a*(1H) 11.6, *a*(1H) 19.0

Where alkenyl and alkynyl esters differ markedly from alkyl and aryl esters is in their reaction with organotin radicals. We found that with photochemically generated trimethyltin radicals, the allyl, **12**, (Figure 7), propynyl, **13**, and pentadienyl radicals, **14**, (Figure 8), were generated from the corresponding sulphonate esters.



The h.f.s of the delocalised radicals formed are shown in Table 3 below, together with the reported literature values.

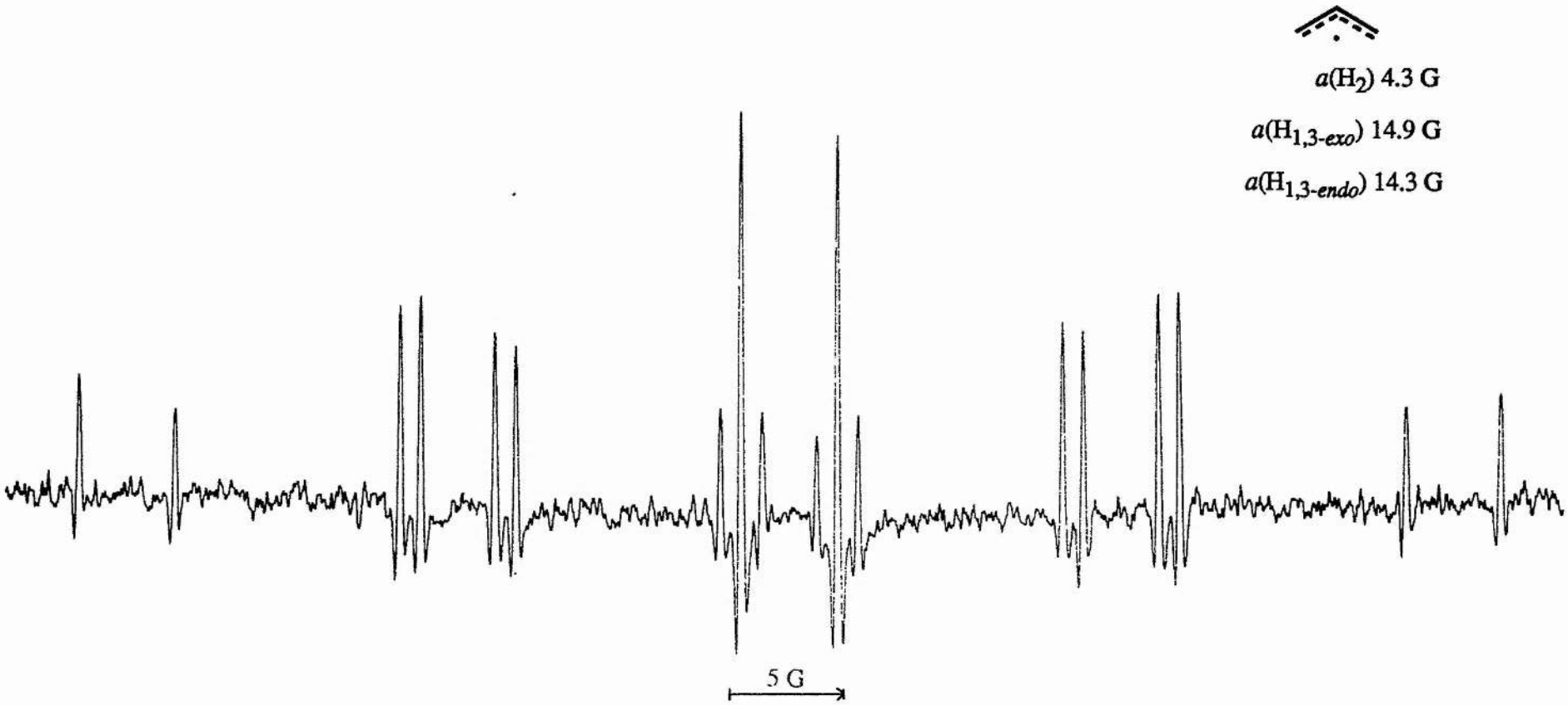


Figure 7. ESR Spectrum Of The Allyl Radical

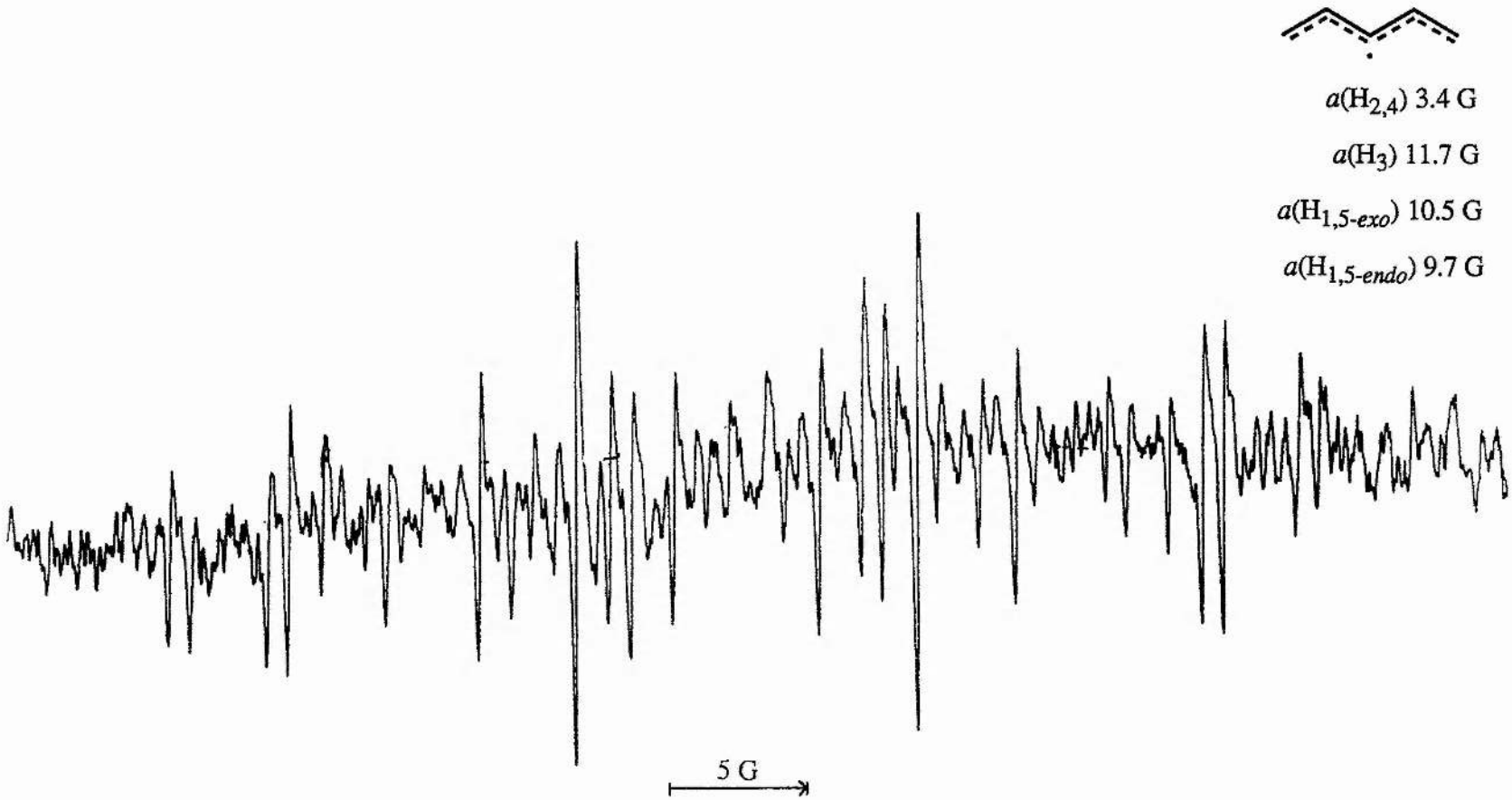


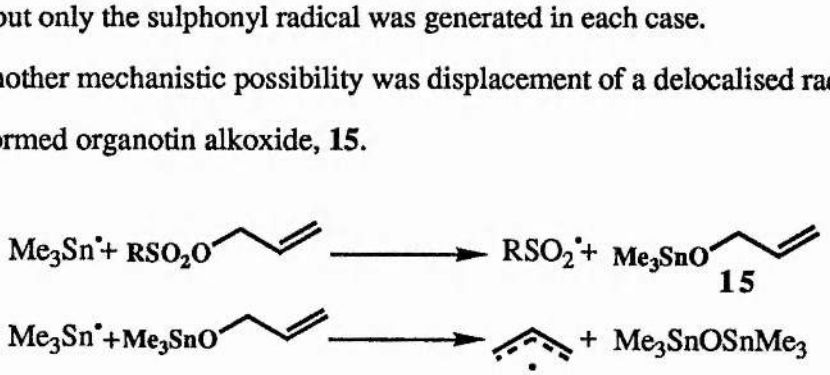
Figure 8. ESR Spectrum Of The Pentadienyl Radical.

Table 3

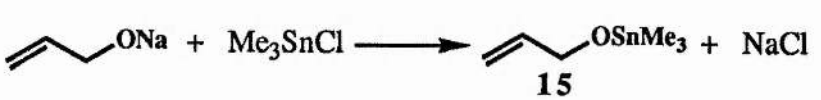
Radical	Observed h.f.s/G	Literature h.f.s/G
	$a(H_{1,3\text{-}exo})$ 14.9, $a(H_{1,3\text{-}endo})$ 14.3, $a(H_2)$ 4.3	$a(H_{1,3\text{-}exo})$ 14.8, $a(H_{1,3\text{-}endo})$ 14.0, $a(H_2)$ 4.53 [192]
	a(1H) 12.65, a(2H) 18.95	a(1H) 12.6, a(2H) 18.9 [193]
	$a(H_{1,5\text{-}exo})$ 10.5, $a(H_{1,5\text{-}endo})$ 9.7 $a(H_{2,4})$ 3.4, $a(H_3)$ 11.7	$a(H_{1,5\text{-}exo})$ 10.4, $a(H_{1,5\text{-}endo})$ 9.6 $a(H_{2,4})$ 3.3, $a(H_3)$ 11.6 [13]

This reaction occurs very readily where R' = CH_3 or $CH(CH_3)_2$, both of which are electron releasing substituents, but does not occur (or rather, is not observable by ESR) where R' = *p*-$CH_3C_6H_4$ or CCl_3, which are electron withdrawing substituents. It was initially considered that the high stability of the delocalised radicals would be the driving force for their formation; the radicals might form *via* cleavage of the R'–O bond. However, this can be ruled out as a possibility as benzyl esters did not give benzyl radicals which are also highly stabilised. Many other sulphonate esters were also examined to investigate whether or not the stability of R was an influencing factor (see Table 1), but only the sulphonyl radical was generated in each case.

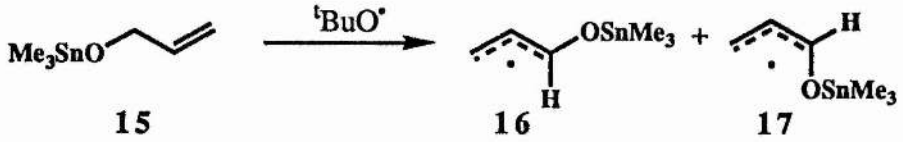
Another mechanistic possibility was displacement of a delocalised radical from the first formed organotin alkoxide, **15**.



An authentic sample of the allyltrimethyltin alkoxide, **15**, was prepared (using a general procedure for preparing organotin alkoxides)[194] from slow addition of trimethyltin chloride to a solution of sodium in allyl alcohol.

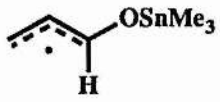


However, this authentic sample of tin alkoxide did not produce any spectroscopically detectable allyl radicals with trimethyltin radicals or on direct photolysis or thermolysis. The reaction of the organotin alkoxide, **15**, with *tert*-butoxyl radicals resulted in hydrogen abstraction to give the *syn*- and *anti*- substituted allyl radicals, **16** and **17**.



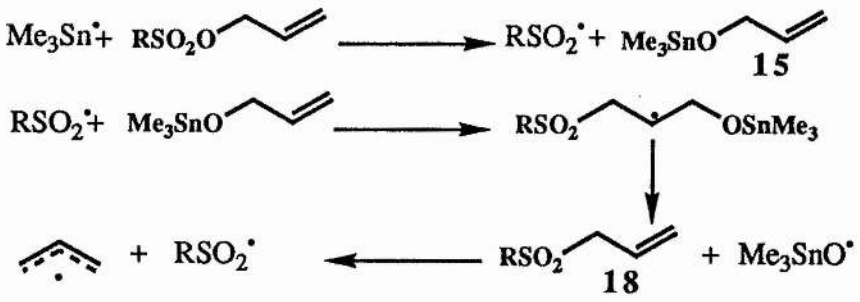
15 **16** **17**

The h.f.s. of the substituted allyl radicals formed are shown below;

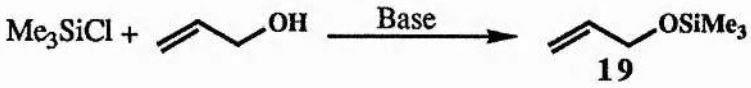
Radical	h.f.s./G
	*a*(1H) 2.8, *a*(2H) 13.3, *a*(1H) 15.8

The spectrum of the *syn*-isomer was weak and overlapped that of the *anti*-isomer and hence could not be unambiguously analysed.

An alternative mechanism which still involves the formation of an organotin alkoxide *via* S_H2 attack of trimethyltin radicals on the ester is outlined below. We propose that sulphonyl radical addition to the organotin alkoxide, followed by β-scission to give the sulphone, **18**, and subsequent displacement of the delocalised radical is the route involved.

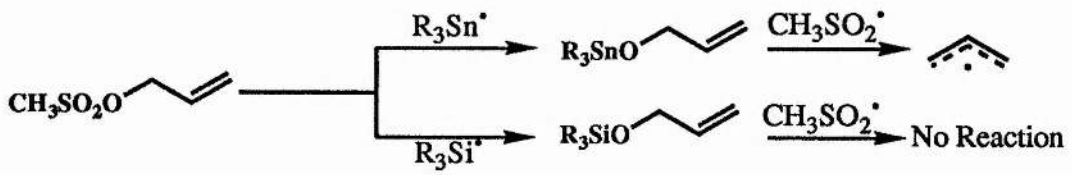


Evidence in support of this mechanism includes the fact that reaction of methanesulphonyl radicals generated from *iso*-propyl methanesulphonate with the authentic organotin alkoxide, was found to produce the allyl radical. Whilst R is important for formation of a delocalised radical, the importance of the trimethyltin radical cannot be disregarded. By analogy with trimethyltin, the triethylsilyl radical also displaces the sulphonyl radical from allyl methanesulphonate which suggests that the triethylsilyl alkoxide forms, but as no allyl radical was detected, the mechanism is assumed to terminate here. Synthesis of trimethylsilyl alkoxide, **19**, was achieved from trimethylsilyl chloride, allyl alcohol and base.

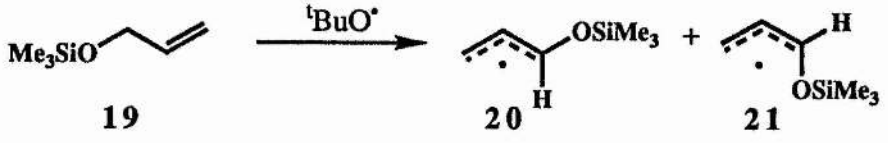


19

Direct photolysis of, or reaction of this alkoxide with tin or sulphonyl radicals failed to generate the allyl radical; this is in agreement with the above experimental findings.

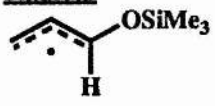


However, hydrogen abstraction occurred from the trimethylsilyl alkoxide, **19**, with *tert*-butoxyl radicals, just as was observed with the tin analogue, to give the *syn*- and *anti*-substituted allyl radicals, **20**, and **21**.



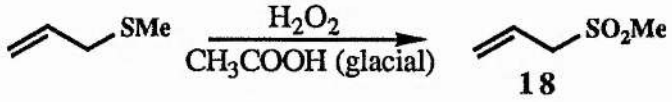
19 **20** **21**

The h.f.s. of the substituted allyl radicals formed are shown below;

Radical	h.f.s./G
	*a*(1H) 3.4, *a*(1H) 13.2, *a*(1H) 14.0, *a*(1H) 14.4

The spectrum of the *syn*-isomer was weak and overlapped that of the *anti*-isomer and hence could not be unambiguously analysed.

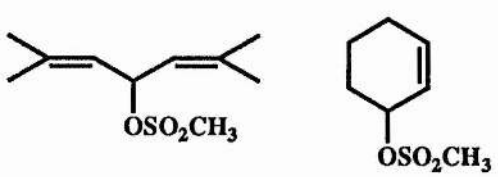
Sulphones are stable species, but is has been reported that allyl and benzyl sulphones can undergo scission to give allyl and benzyl radicals;[195] allyl and benzyl substituents facilitate the homolysis by lowering the C–S bond dissociation energy.[196] An authentic sample of methyl allyl sulphone, **18**, was prepared from methyl allyl sulphide and hydrogen peroxide,[197]



18

but unfortunately no radicals could be generated from this compound under any conditions tried. This may have been due to the low solubility of the sulphone at low temperatures.

As a radical addition reaction is involved this occurs most readily if the unsaturated substituent is terminal. With esters such as **22** and **23** only the sulphonyl radical was observed, even though they were unsaturated and had the potential to form delocalised radicals.

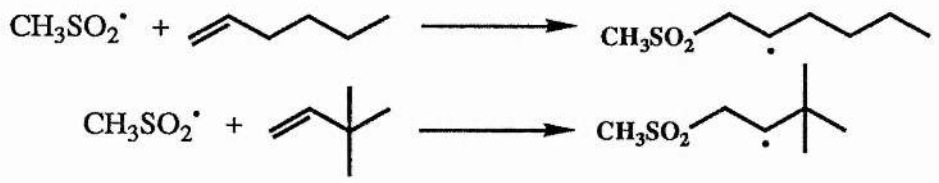


22 **23**

4.4 Sulphonyl Radical-Addition Reactions.

The reaction of sulphonyl radicals with alkenes has been reported previously, but examples are limited and generally confined to aryl sulphonyl radical-addition.

The reaction of the methanesulphonyl radical with a variety of alkenes was attempted and ESR was used to observe any adduct radicals which formed. Simple alkenes underwent addition with sulphonyl radicals, but their adduct spectra were very weak suggesting that the reaction is inefficient.



Conjugation of the alkene did not enhance the quality of the spectra.

The spectrum of the adduct radical obtained was too weak to obtain decent h.f.s. values.

Alkenes with electron donating substituents adjacent to the double bond underwent ready addition with sulphonyl radicals to give comparatively intense spectra. The enhanced reactivity of these alkenes is probably due to the increased electron density in the alkene moiety, supplied by the substituent which leads to a favourable polar effect in the transition state for the electrophilic sulphonyl radicals.

Alkoxy substituents produced the best results and sulphonyl radicals added readily to *n*-butyl- and methyl vinyl ether (see Table 4), (Figure 9).

R' = CH_3, n-C_4H_9

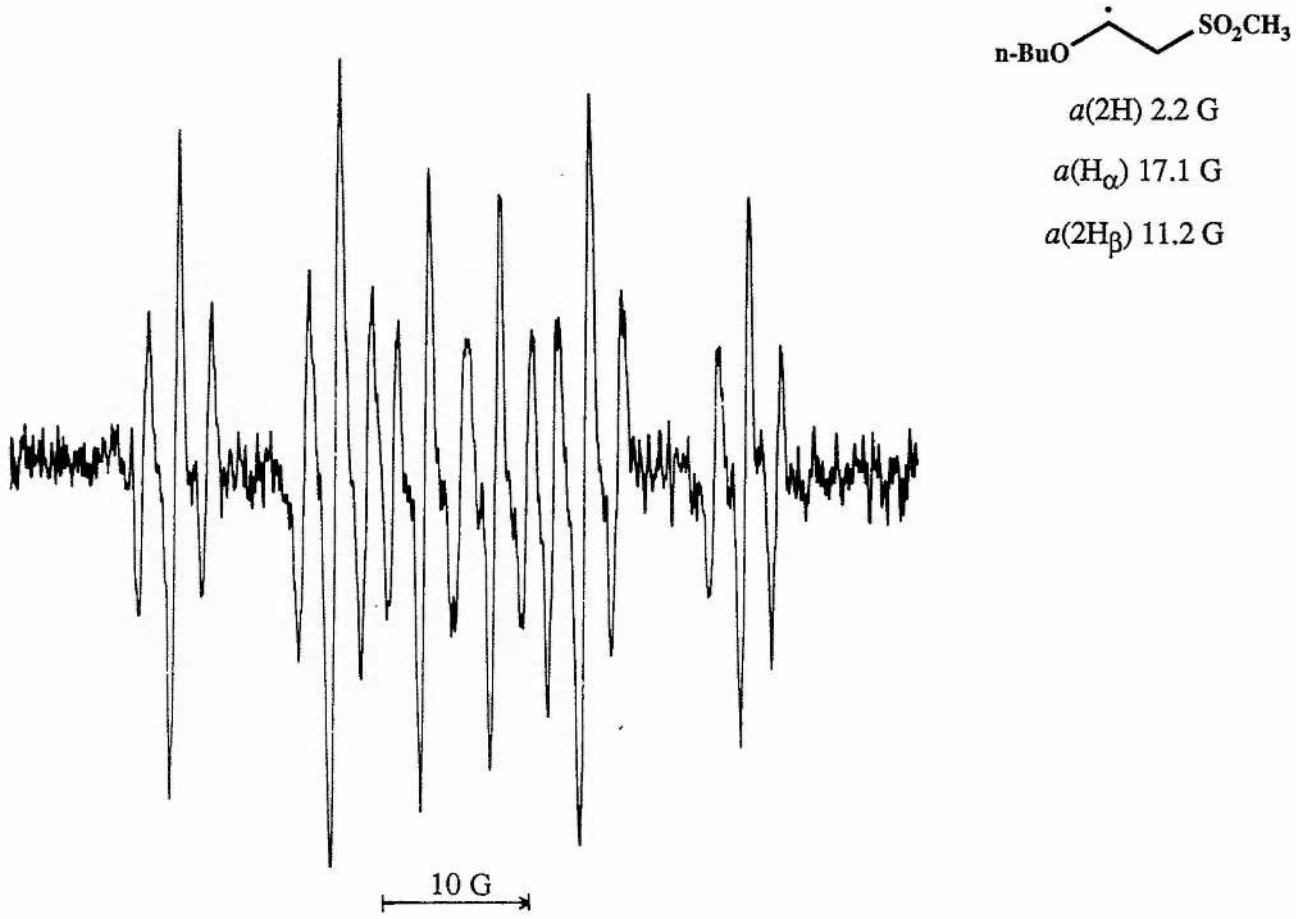
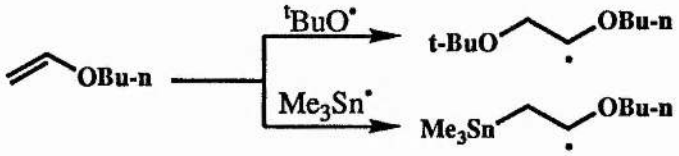
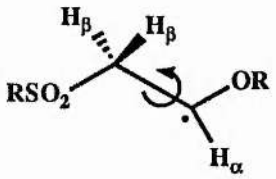


Figure 9. ESR Spectrum Of The Adduct Radical Of *n*-Butyl Vinyl Ether And The MethaneSulphonyl Radical.

That it was sulphonyl addition and not *tert*-butoxyl or trimethyltin radical addition occurring was confirmed by photolysing *n*-butyl vinyl ether with just di-*tert*-butyl peroxide or hexamethylditin. The corresponding adduct radicals from these reactions were very weak, indicating that addition of these species occurs less readily, and their h.f.s were different to those obtained with sulphonyl radical addition.



The ESR spectra of the adduct radicals from sulphonyl radical addition were found to be temperature dependent. This is because restricted rotation can occur about the C_α–C_β bond.



The exchange broadening for this rotation was examined over a range of temperatures, but unfortunately coalescence occurred at too low a temperature to be observed. This was found to be the case for all the alkenes studied in this work.

Good spectra were obtained from alkenes with sulphur centred substituents (see Table 4), however, the spectra were not as strong as with oxygen centred groups, probably because of the different electron donating effects of the two types of groups and also because the phenyl group adjacent to sulphur may help to lower electron density on the alkene.

With a silyl substituent, SiR_3, adjacent to the double bond, addition occurred quite readily.

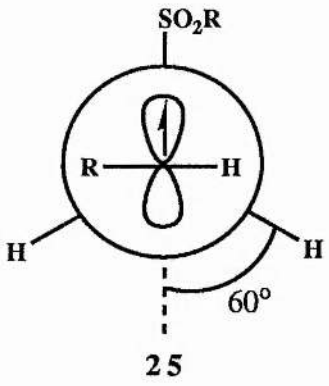
The h.f.s. of the adducts obtained from methanesulphonyl radical addition to alkenes of the type CH_2=CH–R are given below in Table 4.

Table 4.

R	T/K	$a(H_\alpha)$	$a(2H_\beta)$	a(Other)
OBu^n	235	17.1	11.2	2.2 (2H)
OMe	235	17.4	11.0	2.0 (3H)
Bu^t	235	22.4	18.4	–
SPh	235	17.0	11.4	–
$SiMe_3$	235	22.7	17.8	–
$C_4H_9^n$*	215	22.0	13.6	28.0 (2H)

* Tentative Analysis

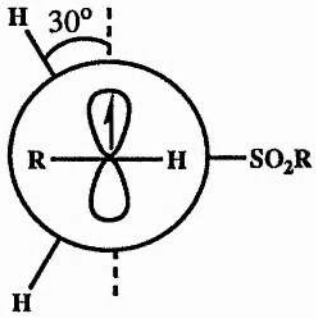
The conformation of the adduct radical can be deduced from the magnitude of the β-h.f.s. values. In the case of R = OBu^n, OMe, $C_4H_9^n$ and SPh, the value tends to be *ca.* 11 G. This indicates that conformer **25** is the preferred rotamer.



25

If this geometry were adopted when bulky substituents were present, *i.e.* R = ^{t}Bu or $SiMe_3$, then steric interaction occurs with the SO_2R group in the adduct, and to lessen the interaction conformer **26** makes a more important contribution to the

average. The magnitude of the β-h.f.s. are temperature dependent because at higher temperatures increased rotation about the C_α–C_β bond allows conformer **26** to become important even in cases where the substituent, R, is not bulky.



26

In this type of orientation, the magnitude of the β-h.f.s. is increased and this is observed in the data in Table 4, where the β-h.f.s. have increased to *ca.* 18 G.

Spectra were weaker for addition to CH_2=CHSiMe$_3$ but after a period of time a second radical, **28**, appeared and then a third radical, **29**. The spectrum of the third radical (see Table 5) became very intense which suggested the formation of a highly stabilised radical. It is known that radicals containing several silyl groups can be highly stabilised by steric effects.[198] The following mechanism may explain the formation of a stabilised radical which corresponds to the ESR spectrum obtained.

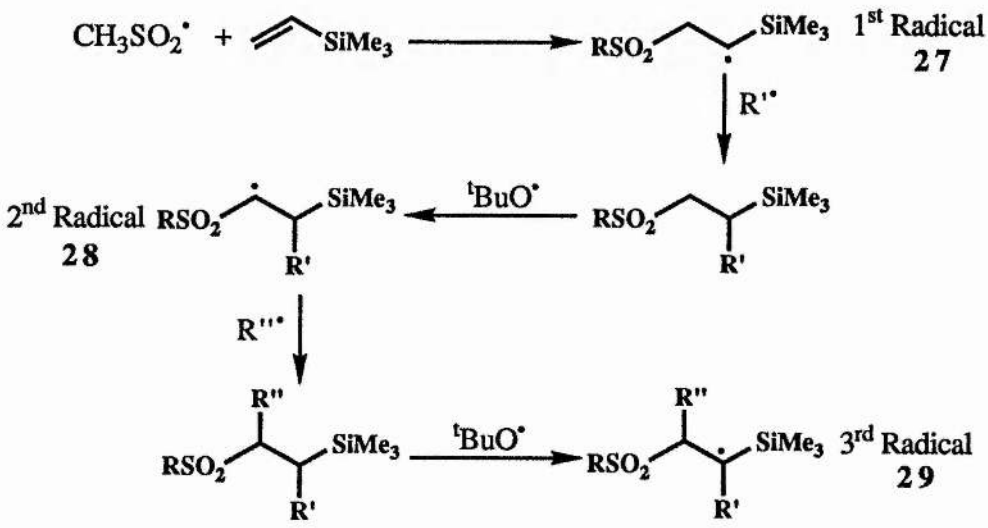
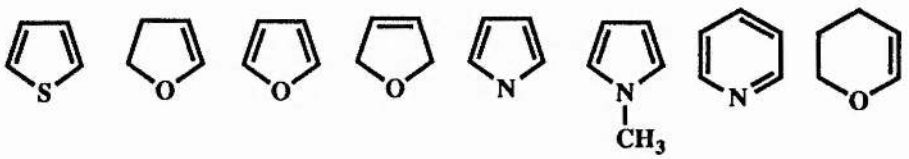


Table 5

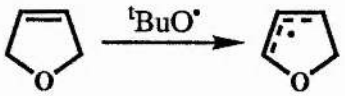
Radical	h.f.s./G
27	*a*(1H) 20.7, *a*(2H) 17.8
28	*a*(1H) 4.5, *a*(1H) 18.6
29	*a*(1H) 17.3

On prolonged photolysis, several other radicals were observed.

It is known that radicals react readily with various heterocyclic molecules such as thiophenes and furans.[199] We carried out reactions of the methanesulphonyl radical with the heterocyclic compounds shown:

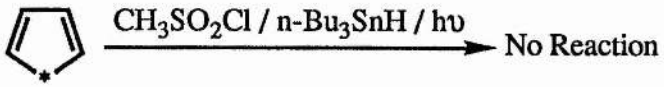


Unfortunately, no adduct radicals were detected by ESR with any of the above heterocyclic molecules, though it was found that the dihydrofuran, **30**, readily underwent hydrogen abstraction to form an allyl type radical, *a*(1H) 2.1, *a*(2H) 13.7, *a*(1H) 37.0, *a*(1H) 37.6.



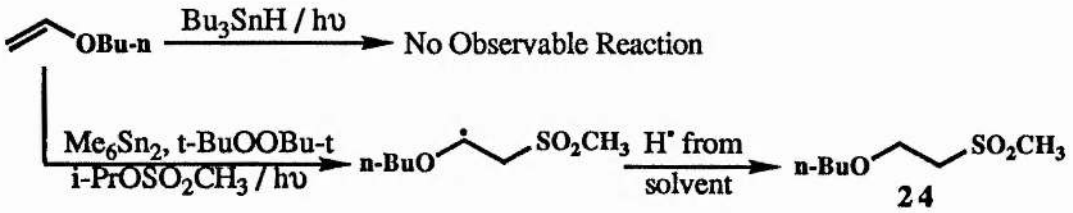
30

Sulphonyl radical additions were also carried out on a preparative scale, but no heterocyclic sulphones were observed.



* = O, S

The addition of sulphonyl radicals (generated from *iso*-propyl methanesulphonate and tri-*n*-butyltin hydride) to *n*-butyl vinyl ether has been carried out on a preparative scale and the corresponding sulphone, **24**, was identified in the mixture, though the addition product of the *tert*-butoxyl radical was also present.



These reactions show the advantage of using sulphonate esters as radical precursors rather than sulphonyl chlorides because, when *n*-butyl vinyl ether was added to methanesulphonyl chloride, a black tar was produced in seconds.

4.5 Experimental

General method for the preparation of alkane- and trihaloalkane-sulphonate esters.

To a solution of the alcohol (1 mol. equiv.) and triethylamine (1 mol. equiv.) in dry methylene chloride at 0 °C under N_2 was added the corresponding sulphonyl chloride (1.1 mol.equiv.) dropwise. The mixture was then stirred for 45 min. The organic layer was then washed (water, dil. hydrochloric acid, water, sat. NaCl. aq.), dried ($MgSO_4$ anhyd.) and evaporated. The alkanesulphonate esters were used without any further purification. This method was used in the preparation of methane-, *iso*-propane-, trifluoromethane-, and trichloromethanesulphonate esters.

Confirmation that the sulphonate ester had formed was carried out by IR spectroscopy. Absorption bands at *ca.* 1380-1347 and 1193-1170 cm^{-1} indicated that the ester had formed.

General method for the preparation of *p*-toluenesulphonate esters.

To a solution of the alcohol (1 mol. equiv.) and dry pyridine (1 mol. equiv.) in dry methylene chloride at 0 °C under N_2 was added solid *p*-toluenesulphonyl chloride (1.1 mol. equiv.) in small portions. After stirring for 1 hr. the mixture was allowed to stand at 0 °C for 24 hr. The organic layer was then washed (water, dil. hydrochloric acid, water, sat. NaCl. aq.), dried ($MgSO_4$ anhyd.) and evaporated. The *p*-toluenesulphonate esters were used without any further purification.

Reduction of *iso*-propyl *p*-toluenesulphonate to *p*-toluenesulphinic acid with tri-*n*-butyltin hydride.

To *iso*-propyl *p*-toluenesulphonate (0.3 g; 1.40 mmol) in *tert*-butylbenzene was added tri-*n*-butyltin hydride (0.37 cm^3; 1.40 mmol). An exothermic reaction began immediately. The solution was then heated to 140 °C and photolysed for 2 hr, after which the mixture was cooled and diluted with ether and 2 M NaOH solution. The

aqueous layer was removed and acidified (conc. HCl, pH paper) before re-extracting with ether (x2). The combined ether layers were dried (Na_2SO_4 anhyd.) and evaporated to give *p*-toluenesulphinic acid as a white solid. δ_H 2.34 (3H, s, CH_3), 6.95-7.58 (4H, m, aromatic), 10.14 (1H, s, $SO_2\underline{H}$).

Trimethylsilylmethanesulphonyl chloride.[187,188]

Chloromethyltrimethyl silane (4.0 g; 32.6 mmol) and thiourea (5.1 g; 67.0 mmol) in ethanol (58 cm^3) were refluxed for 48 hr. The solution was then evaporated to dryness and pumped at 1 mmHg for 1 hr. The isothiouronium salt formed was dissolved in water (70 cm^3), and cooled to 0 °C. Chlorine gas was then bubbled through the solution for 15 min.with stirring, keeping the temperature below 10 °C. Methylene chloride was added (50 cm^3) and chlorine was bubbled for a further 45 min., after which the organic layer was removed and the aqueous re-extracted (x2). The combined organic layers were washed (10% $NaHSO_3$ aq.,10% $NaHCO_3$ aq. and water), dried ($MgSO_4$ anhyd.) and evaporated.The product was distilled by kugelrohr (60-90 °C/ 1 mmHg; Lit.[187,188] 50-52 °C/ 0.6 mmHg) Yield 0.6 g; 10%. (Lit.[187,188]) δ_H 0.32 (9H, s, CH_3), 3.63 (2H, s, CH_2). δ_C -1.16 (CH_3), 59.91 (CH_2). *m/z* 186 (M^+, 1), 171 (2), 141 (4), 137 (9), 123 (6), 93 (15), 73 (100), 58 (7), 45 (18).

Trimethyl(2-propenyloxy)stannane.

Sodium metal (0.25 g; 10.9 mmol) was dissolved (in small pieces) in allyl alcohol (5 cm^3) at 0 °C under N_2. To this, was added a solution of trimethyltin chloride (2.17 g; 10.9 mmol) in allyl alcohol (5 cm^3) in small portions. The mixture was stirred for 30 min. at 0 °C then centrifuged. The clear supernatant liquid was carefully removed from the solid deposit of sodium chloride and evaporated to give the product. The product was distilled by kugelrohr (85 °C/ 14 mmHg) to give a clear colourless liquid. Yield 0.9 g; 37%. δ_H 0.44 (9H, s, $Sn(CH_3)_3$); 4.17 (2H, br d, CH_2); 4.99-5.29 (2H, br dd, CH_2); 5.86-6.06 (1H, m, CH). δ_C -1.94 (CH_3), 65.09 (CH_2), 114.60 (CH_2), 138.49 (CH). Between 298 and 373 K the ^{13}C NMR spectrum showed

line-broadening. This was resolved into conventional sharp peaks at 273 and 233 K.

Trimethyl(2-propenyloxy)silane.

To a solution of allyl alcohol (6.0 g; 0.103 mol), and pyridine (8.2 g; 0.104 mol), in 40-60 °C petroleum ether (40 cm^3) under N_2 was added trimethylsilyl chloride (11.24 g; 0.103 mol) dropwise. The mixture was stirred for 45 min. before filtering off the white precipitate of pyridine hydrochloride. The solution was then distilled on a Vigreux column, the solvent distilling over first, followed by the product (100-101 °C/ 760 mmHg; Lit.[200] 95-96 °C/ 760 mmHg). Yield 2.6 g; 20%. (Lit.[200]) δ_H 0.11 (9H, s, CH_3), 4.08 (1H, d, CH_2), 4.87-5.40 (2H, m, CH_2), 5.58-6.26 (1H, m, CH).

Methyl allyl sulphone.[197]

Methyl allyl sulphide (6.0 g; 68.0 mmol) in glacial acetic acid (14 cm^3) was chilled in ice. 30% hydrogen peroxide solution was added dropwise and the mixture allowed to stir overnight. The solution was then heated at 85 °C for 1 hr. then cooled and diluted with an equal volume of water. The aqueous solution was then extracted with methylene chloride (x2). The combined organic layers were washed (water), dried (Na_2SO_4 anhyd.), evaporated under reduced pressure and distilled by kugelrohr (135 °C/ 1 mmHg). Yield 5.45 g; 67%. (Lit.[201]) δ_H 3.00 (3H, s, CH_3), 3.82 (2H, br d, CH_2), 5.24-6.42 (3H, m, $CH=CH_2$).

Reaction of methanesulphonyl radicals with *n*-butyl vinyl ether using tri-*n*-butyltin hydride under photolysis conditions.

To a degassed solution of *iso*-propyl methanesulphonate (0.3 g; 2.17 mmol) and *n*-butyl vinyl ether (0.22 g; 2.17 mmol) in *tert*-butylbenzene at 65 °C was added tri-*n*-butyltin hydride over 30 min. whilst photolysing the solution. The mixture was then photolysed at this temperature for 9 hr. Analysis of the mixture showed unreacted *iso*-propyl methanesulphonate ester and none of the expected sulphone.

Reaction of methanesulphonyl radicals with *n*-butyl vinyl ether using hexamethylditin and di-*tert*-butyl peroxide as initiator.

A degassed solution containing roughly equal volumes of *n*-butyl vinyl ether, hexamethylditin, di-*tert*-butyl peroxide and *iso*-propyl methanesulphonate in toluene was photolysed for 8 hr. at room temperature. Analysis of the mixture by GC/MS appeared to show the adducts formed from *tert*-butoxyl radical addition and methanesulphonyl radical addition.

Chapter Five

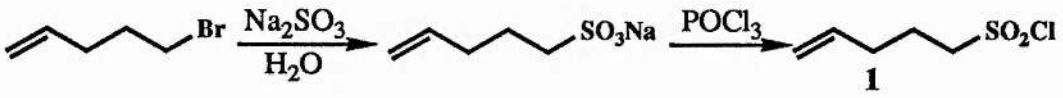
Sulphonyl Radical Cyclisation

5.1 Cyclisation Of Sulphonyl Radicals.

In view of the high reactivity of sulphonyl radicals towards alkenes, it is surprising that the intramolecular cyclisation of unsaturated sulphonyl radicals, which is a potential route to cyclic sulphones, has scarcely been investigated.

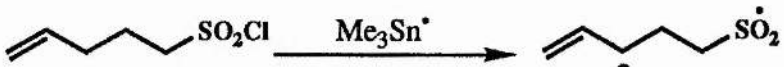
5.2 Pentenesulphonyl Radical.

By analogy with the well studied hex-5-enyl radical, the archetypal pent-4-ene-1-sulphonyl radical was generated from the corresponding pent-4-ene-1-sulphonyl chloride, **1**, which in turn was prepared from 5-bromopent-1-ene using sodium sulphite and phosphorus oxychloride.[202]



1

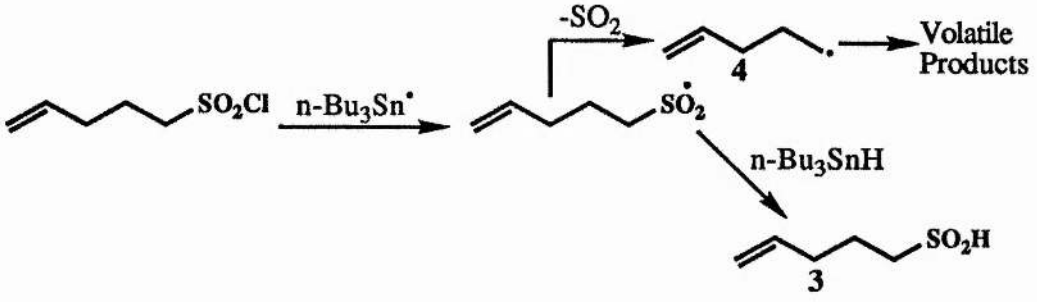
Treatment of pentenesulphonyl chloride with photochemically generated trimethyltin radicals in the cavity of an ESR spectrometer gave the spectrum of the pent-4-ene-1-sulphonyl radical, **2**, ($a(2H_\alpha)$ 0.5, $a(2H_\beta)$ 2.5), which was observed over the temperature range 240-370 K, but no cyclised species were detected at these or higher temperatures.



2

Reduction of pentenesulphonyl chloride with tri-*n*-butyltin hydride using photochemical initiation at temperatures between 105-170 °C, gave pentenesulphinic acid, **3**, as the only detectable product. This was produced when the pentenesulphonyl

radical abstracted hydrogen from the tri-*n*-butyltin hydride. Loss of SO_2 probably also occurred, but the volatile products derived from **4** were not observed.



No reaction occurred when pent-4-ene-1-sulphonyl chloride was photolysed at 170 °C in the absence of an initiator. However, treatment of pentenesulphonyl chloride with a variety of alternative radical initiator systems led to the formation of 3-chlorotetrahydrothiopyran-1,1-dioxide as the major product. In certain cases, tetrahydrothiopyran-1,1-dioxide and 2-chloromethyltetrahydrothiophene-1,1-dioxide were obtained as minor components.

The copper chloride-catalysed addition of sulphonyl chlorides to alkenes (Asscher-Vofsi reaction)[121] has long been known as a general and convenient synthesis of β-chlorosulphones and, by dehydrohalogenation, of α,β-unsaturated sulphones. The copper chloride-catalysed system differs from a general radical addition reaction in that a redox-transfer mechanism is involved.

Using conventional radical initiator systems, the addition of a sulphonyl chloride to an alkene would follow the mechanism outlined below:

$$X^{\bullet} \text{ (from initiator)} + RSO_2Cl \longrightarrow XCl + RSO_2^{\bullet}$$

$$RSO_2^{\bullet} + CH_2{=}CHR' \rightleftharpoons RSO_2CH_2\dot{C}HR' \quad (1)$$

$$RSO_2CH_2\dot{C}HR' + RSO_2Cl \rightleftharpoons RSO_2CH_2CHClR' + RSO_2^{\bullet} \quad (2)$$

It is usually assumed that the redox-transfer mechanism completely supersedes the transfer step (2) by the following reduction-oxidation steps which lead to the same

overall result as (2).

$$RSO_2CH_2\dot{C}HR' + CuCl_2 \longrightarrow RSO_2CH_2CHClR' + CuCl$$

$$CuCl + RSO_2Cl \rightleftharpoons CuCl_2 + RSO_2^{\bullet}$$

The failure of aliphatic sulphonyl chlorides to react well with alkenes using more usual radical initiator systems is attributable to their low reactivity in step (2). In all the cyclisation reactions discussed here, the use of copper chloride as a catalyst resulted in a more rapid and more efficient cyclisation. The ready addition of such sulphonyl chlorides under copper chloride catalysis is due to the covalently bound chlorine on the sulphonyl moiety being effectively activated by the redox transfer.

Copper (II) chloride is always used in conjunction with triethylamine hydrochloride or trialkylammonium chlorides, which have been shown to have a marked effect upon the reaction for the following reasons:

(i) Copper (II) chloride forms trialkylammonium chlorocuprates with triethylammonium chloride which are more soluble in solvents such as chloroform or methylene chloride than copper (II) chloride itself. The copper (I) chloride formed during the reaction is also kept in solution for the same reasons.

(ii) At least one chloride ion must remain in the copper (II) co-ordination sphere, in order for the ligand transfer step to occur.

$$RSO_2CH_2\dot{C}HR' + CuCl_2 \longrightarrow RSO_2CH_2CHClR' + CuCl$$

Excess of chloride ion also completely suppresses telomerisation of copper catalysed addition of sulphonyl chlorides to alkenes.

(iii) Excess chloride ion suppresses the solvolysis of copper (II) chloride by solvent (*e.g.* acetonitrile) or substrate. Addition of a sulphonyl chloride to acrylonitrile in the absence of triethylammonium chloride causes a drastic drop in yield as acrylonitrile (AN) forms a complex with copper (II). Excess chloride ion, therefore, displaces the

solvolysis equilibrium to the left.

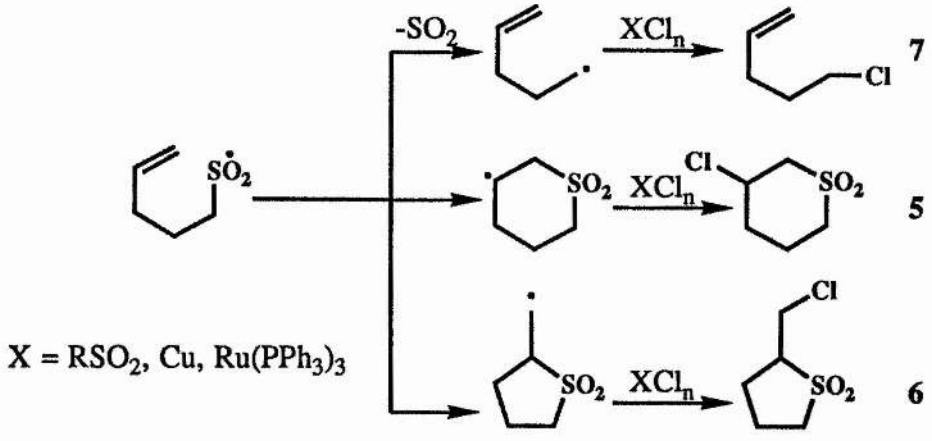
$$CuCl_2 + nAN \longrightarrow Cu(AN)_n^{2+} + 2Cl^-$$

In the reaction of pent-4-ene-1-sulphonyl chloride the chlorinated six-membered ring sulphone, **5**, was always the predominant isomer, but varying the temperature altered the relative proportion of **5** and the five-membered ring sulphone, **6**. The overall yield of product tended to be low but this is probably due to several competing side reactions.

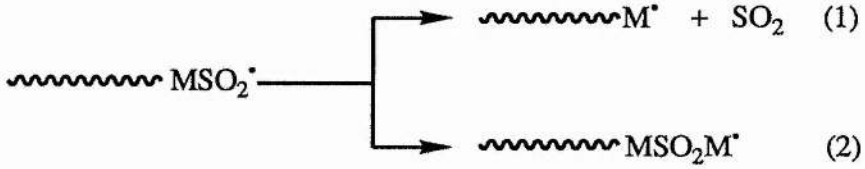
Firstly, it is known that sulphonyl radicals can undergo an α-scission process, namely:[116]

$$RSO_2^{\bullet} \longrightarrow R^{\bullet} + SO_2$$

This will be very important at 150 °C where many of the reactions were carried out. With the pentenesulphonyl radical, α-scission would lead to the pentenyl radical which would then abstract chlorine from either copper chloride or sulphonyl chloride to give 5-chloropentene, **7**. Being a volatile component, chloropentene would evaporate under the reaction conditions used, thus reducing the overall yield. In low temperature reactions (*ca.* 75 °C) between pentenesulphonyl chloride and copper chloride, the reaction mixture was found to contain significant amounts of chloropentene.

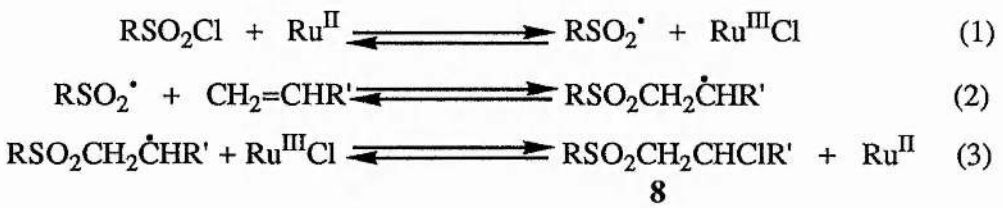


Secondly, a significant amount of material may polymerise. It is known that sulphur dioxide and vinylic monomers (both of which are present if α-scission of the pentenesulphonyl radical occurs) can readily undergo co-polymerisation. In fact, sulphonyl radical polymerisation has attracted interest in that one of the peculiar features of the reaction is that the growing sulphonyl radical may undergo depropagation (1) as well as propagation (2).[203]



Polymerisation was believed to occur with the pentenesulphonyl chloride as the cyclised products had to be extracted by preparative TLC out of a black, viscous, intractable tar which was probably polymerised material.

A second transition metal chloride to have found use in the addition of sulphonyl chlorides to alkenes is dichlorotris (triphenylphosphine) ruthenium (II). Once again, a free radical redox-transfer mechanism is believed to be involved.[136]



8

The ruthenium catalyst first abstracts a chlorine atom from the sulphonyl chloride to generate the sulphonyl radical and the ruthenium (III) species (eq. 1). The sulphonyl radical then attacks the alkene to give an intermediate radical (eq. 2) which then abstracts the chlorine from ruthenium (III) chloride to give the β–chlorosulphone adduct, **8**. All three steps are believed to be in equilibrium, and it has been reported that the equilibrium lies well to the left because no β-chlorosulphone is found in the absence of a tertiary amine. The role of the tertiary amine is to promote dehydrohalogenation of

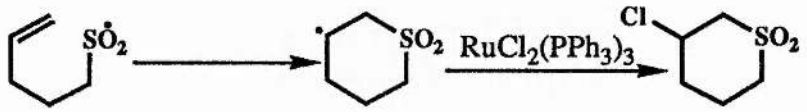
the β-chlorosulphone to the α,β-unsaturated sulphone, **9**, as shown below;

$$RSO_2CH_2CHClR' + Et_3N \longrightarrow \underset{\mathbf{9}}{RSO_2CH{=}CHR'} + Et_3N.HCl$$

The resulting triethylamine hydrochloride precipitates out of solution, thus shifting the equilibrium towards the final products (α,β-unsaturated sulphone, **9**, and $Et_3N.HCl$).

A second possible mechanism involving oxidative addition of the alkene sulphonyl chloride to form a ruthenium (IV) complex and subsequent elimination of the ruthenium complex hydrochloride [$HRu^{IV}Cl$], was considered to be much less probable since the conversion of Ru (II) to Ru (IV) should be very difficult.

Whilst the use of dichlorotris (triphenylphosphine) ruthenium (II) required a higher temperature than copper chloride in order for it to initiate a radical reaction with pentenesulphonyl chloride, it was found totally unnecessary to use a tertiary amine to move the equilibrium to the right. Cyclisation was found to occur at 170 °C to give the six-membered ring sulphone as the only observable product.



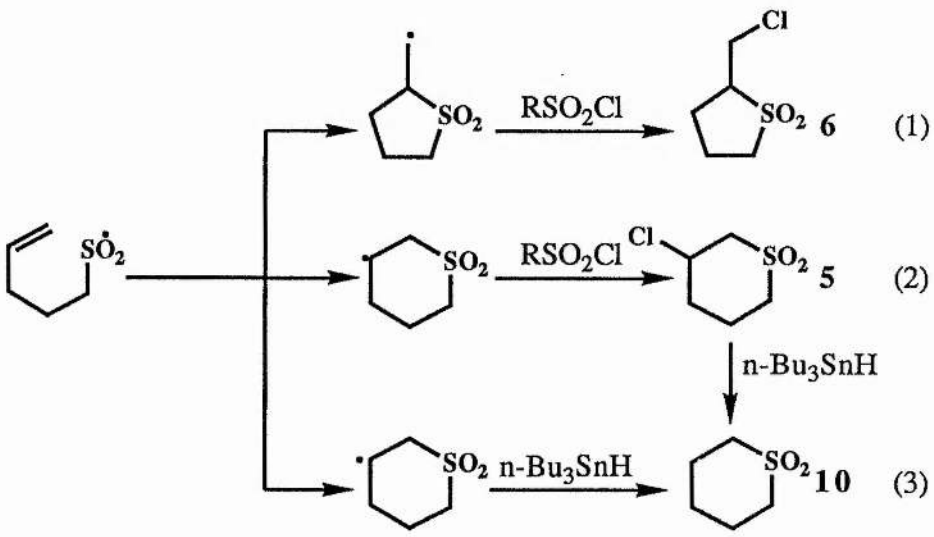
Other transition metal chlorides have been reported in the literature, which catalyse intermolecular sulphonyl radical addition, but with a much lower degree of success. Use of stoichiometric amounts of iron (II) chloride produces sulphinic acids from sulphonyl chlorides under free radical conditions.[121]

$$C_6H_5SO_2^{\bullet} + Fe^{2+} \longrightarrow C_6H_5SO_2^{-} + Fe^{3+}$$

Whilst the reaction of photochemically generated tri-*n*-butyltin radicals with pentenesulphonyl chloride led exclusively to the sulphinic acid, a much milder reaction

was achieved by using tri-*n*-butyltin hydride with AIBN as the initiator. The milder conditions allowed ring closure of the pentenesulphonyl radical to occur before it subsequently abstracted a hydrogen atom from the tin hydride to give the sulphinic acid.

Cyclisation using tri-*n*-butyltin hydride gave rise to three cyclised products, 3-chlorotetrahydrothiopyran-1,1-dioxide, **5**, 2-chloromethyltetrahydrothiophene-1,1-dioxide, **6**, and tetrahydrothiopyran-1,1-dioxide, **10**. Surprisingly the chlorinated six-membered ring sulphone was the major product rather than the non-chlorinated sulphone. This suggests that chlorine atom transfer must occur very rapidly from the sulphonyl chloride



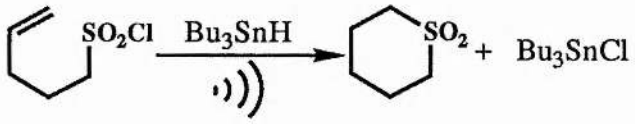
i.e. reaction (2) must compete effectively with hydrogen atom transfer from tri-*n*-butyltin hydride, which is known to be very fast.[204]

The small amount of non-chlorinated product occurs *via* reaction (3) and also by tin hydride reduction of 3-chlorotetrahydrothiopyran-1,1-dioxide. This last step was confirmed by reaction of the chlorinated sulphone with tri-*n*-butyltin hydride to give tetrahydrothiopyran-1,1-dioxide as the sole product. However, if the reaction is carried out at lower temperatures (*ca.* 45 °C) then the major product is tetrahydrothiopyran-1,1-dioxide, which suggests that at these temperature hydrogen abstraction competes

more effectively with chlorine atom transfer from sulphonyl chloride.

Irradiation of homogeneous liquids with ultrasound creates localised superheated cavities, wherein a maximum temperature of over 2000 K can be realised. High intensity ultrasound has been reported to smoothly initiate the selective thermolysis of tin hydride, even at temperatures below 0 °C. The high level of observed product selectivities indicates that the dominant fraction of the reaction product has been formed in the cold bulk liquid phase and not in the hot cavities. In contrast to the normal thermal conditions, wherein both the initiation and propagation steps necessarily take place under an identical thermal environment, the sonochemical conditions permit these steps to be carried out under very different thermal conditions.[205]

The reaction of tri-*n*-butyltin hydride and pent-4-ene-1-sulphonyl chloride at room temperature in the presence of ultrasound generated the pentenesulphonyl radical which cyclised to give tetrahydrothiopyran-1,1-dioxide as the sole product.



This observation agrees with the others obtained and hence it can be deduced that with tri-*n*-butyltin hydride;

(i) Photochemical initiation at elevated temperatures (it proved ineffective at low temperatures) gives rise to the sulphinic acid as the sole non-volatile product.

(ii) Initiation with AIBN at 80 °C gives predominantly the chlorinated cyclic sulphone.

(iii) Initiation with AIBN at 40-50 °C gives predominantly the non-chlorinated cyclic sulphone but the reaction is inefficient as the AIBN does not decompose rapidly enough at these temperatures.

(iv) Initiation with ultrasound at room temperature gives the non-chlorinated cyclic sulphone as the sole product, the tri-*n*-butyltin radical being efficiently generated by

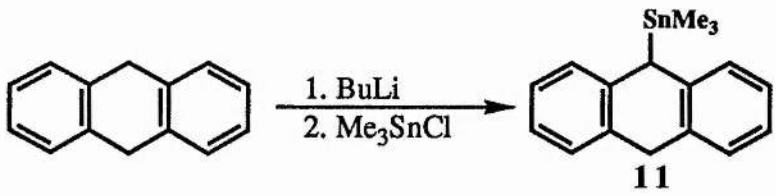
ultrasonification even at low temperature.

Removal of tin residues proved particularly difficult. Reaction of the residue with KF/I_2[206,207] solution enabled most of the tin to be removed, but some still remained. The only efficient method to remove all of the tin residues was by preparative TLC.

Because yields of cyclised sulphones were low and the tin residues difficult to remove, we sought a new initiator system which would deliver hydrogen more slowly in the second propagation step, thus allowing more time for cyclisation.

Recently, triphenylsilane has been reported as an alternative to tri-*n*-butyltin hydride as a radical initiator.[208] Hydrogen abstraction from silane is much slower than that from tin hydride, hence the pentenesulphonyl radical cyclisation can compete effectively with hydrogen abstraction. In fact, hydrogen abstraction was found to be rather sluggish and even after prolonged photolysis at 170 °C a mixture of pentenesulphonyl chloride and triphenylsilane was still only partly reacted. However, three cyclised products were observed in roughly equivalent proportions to that found with the analogous tin hydride.

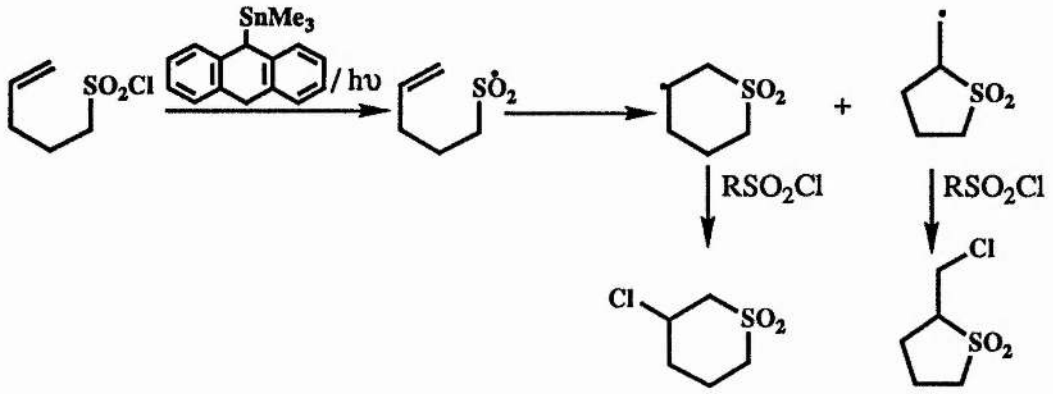
Secondly, it has recently been reported that 9-trimethylstannyl-9,10-dihydroanthracene, **11**, is often a useful substitute for tri-*n*-butyltin hydride as a source of organotin radicals.[209] Use of this compound overcomes the problem of rapid hydrogen abstraction with tin hydrides, R_3SnH. This unusual organotin compound is easily prepared from dihydroanthracene and trimethyltin chloride.[209]



11

Hydrogen abstraction is normally from the solvent when using this tin radical precursor, but the reaction between pentenesulphonyl chloride and trimethylstannyl

dihydroanthracene was carried out without solvent at 170 °C; cleavage to give the trimethyltin radical being achieved by photolysis. Absence of a suitable hydrogen donor led to the production of chlorinated cyclised sulphones.



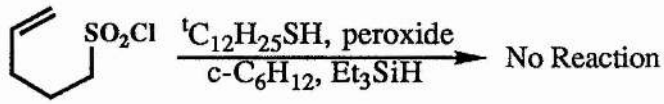
Hexa-*n*-butylditin works in an analogous way to the trimethylstannyl dihydroanthracene just described in that it relies on hydrogen abstraction from the solvent. Hexa-*n*-butylditin and AIBN with pentenesulphonyl chloride were heated in benzene solution. Cyclisation was observed to occur readily over a range of temperatures and three cyclic sulphones were detected.

It has been shown that thiols act as polarity reversal catalysts in hydrogen atom transfer from organosilanes to alkyl radicals.[210] Using such a catalyst, triethylsilane reduces alkyl halides to alkanes under mild conditions *via* the following reactions.

$$Et_3Si^{\bullet} + RX \longrightarrow Et_3SiX + R^{\bullet}$$
$$R^{\bullet} + R'SH \longrightarrow RH + R'S^{\bullet}$$
$$R'S^{\bullet} + Et_3SiH \longrightarrow R'SH + Et_3Si^{\bullet}$$

The success of the above reaction at reducing alkyl halides prompted us to attempt the reaction with pent-4-ene-1-sulphonyl chloride to observe whether formation of cyclic sulphones could be achieved. Reaction of pent-4-ene-1-sulphonyl chloride, *tert*-dodecanethiol, triethylsilane and dilauroyl peroxide in refluxing cyclohexane

proved fruitless.

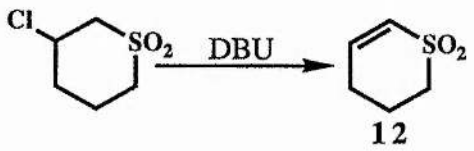


The sulphonyl chloride remained unreacted and so it may be concluded that the above catalysis scheme is not effective in the reduction of sulphonyl chlorides.

The reaction of pent-4-ene-1-sulphonyl chloride with dibenzoyl peroxide at 170 °C was attempted, but analysis of the reaction mixture showed that no reaction had occurred.

Whilst not attempted, the action of tris(trimethylsilyl)silane on pent-4-ene-1-sulphonyl chloride should bring about a free radical cyclisation. Tris(trimethylsilyl)silane has been reported to be an effective substitute for toxic tri-*n*-butyltin hydride in free radical chain reductions.[211]

Dehydrochlorination of 3-chlorotetrahydrothiopyran-1,1-dioxide with DBU gave dihydrothiopyran-1,1-dioxide.

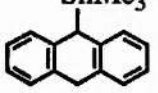


12

The results obtained with pent-4-ene-1-sulphonyl chloride and the various radical initiator systems used are summarised below;

Table

Products of Radical Reactions of Pent-4-ene-1-sulphonyl Chloride.

Initiator	T/°C	Yield[a] mol %	Rel. Yields (%)		
			5	10	6
$CuCl_2$/AIBN	150	17	100	–	–
"	75	nd	88	–	12
$RuCl_2(Ph_3P)_3$	170	15	100	–	–
Bu_3SnH/AIBN/C_6H_6	80	nd	74	26	–
Bu_3SnH/AIBN/C_6H_6	45	nd	20[b]	80[b]	–
Bu_3SnH/C_6H_6/ultrasound	20	nd	–	100	–
$(Bu^n{}_3Sn)_2$/AIBN/$PhBu^t$	45	nd	77	12	11
Ph_3SiH/hυ	170	nd	78	14	8
 /hυ	170	18	91	–	9

[a] Yield of cyclised products after prep. TLC. nd = not determined.

[b] Very approximate.

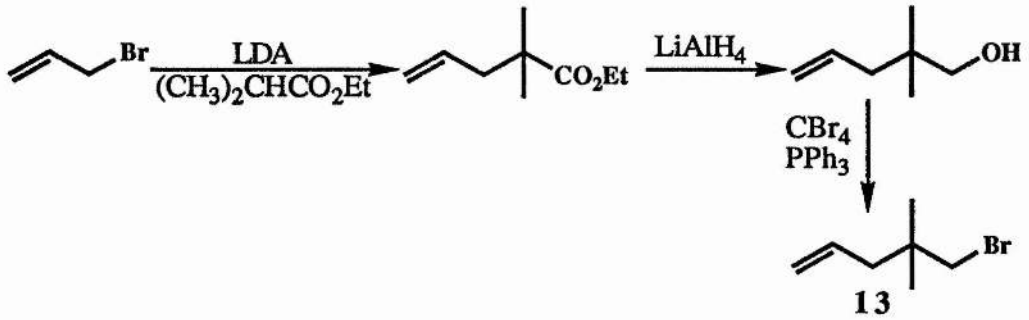
5.3 Cyclisation Of Sulphonate Esters.

The successful method of generating sulphonyl radicals from sulphonate esters as described in Chapter Four should also be applicable to the pent-4-ene-1-sulphonyl radical. *Iso*-propyl pent-4-ene-1-sulphonate was prepared from pent-4-ene-1-sulphonyl chloride and *iso*-propanol. Initially attempts were made to generate the radical in the cavity of an ESR spectrometer using photochemically generated trimethyltin radicals. Unfortunately, no radicals were detected within the accessible temperature range.

Use of a sulphonate ester on a preparative scale should lead exclusively to non-chlorinated cyclic sulphones and therefore this reaction was also examined by product analysis. However, reaction of the ester with tri-*n*-butyltin hydride (photolysis or AIBN initiation) or dibenzoyl peroxide proved fruitless and only the unreacted sulphonate ester was detected in the reaction mixture. It is unknown why formation of and subsequent cyclisation of the pent-4-enesulphonyl radical does not occur.

5.4 Substituted Pentenesulphonyl Radicals.

It was decided to investigate the cyclisation of some substituted pent-4-enesulphonyl radicals so as to compare substituent effects. We attempted, therefore, to prepare 3,3-dimethylpent-4-ene-1-sulphonyl chloride. The preparative route to the bromide is outlined below;



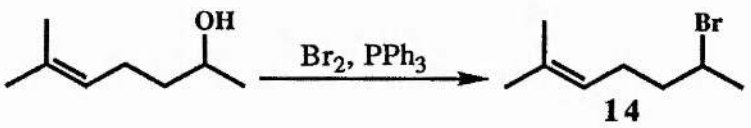
13

The enolate of ethyl *iso*-butyrate was prepared by adding a solution of it in HMPT to lithium di-*iso*-propylamide.[212] The use of HMPT as a solvent enables better release of the lithium anion. Subsequent addition of allyl bromide gave the ester, ethyl 2,2-dimethylpent-4-enoate.[213] This was reduced to the alcohol using lithium aluminium hydride[214] and then brominated using carbon tetrabromide.[215] Unfortunately, after repeated attempts, including prolonged reaction time and increased temperature, the bromide, **13**, would not react with sodium sulphite to give the sodium salt of the sulphinic acid, and hence the sulphonyl chloride was not prepared. The unreactive nature of the bromide may well be due to the *gem*-dimethyl effect.[216,217] Compounds possessing a *gem*-dimethyl moiety often behave differently in their reactivity towards other reactants by virtue of the steric effect of the methyl substituents.[218]

As this proved unsuccessful, it was decided to prepare the mono-methyl analogue, 2-methylpent-4-ene-1-sulphonyl chloride. The bromide could be prepared by a similar route to that of the dimethyl ester. Reaction of the enolate of methyl propionate with allyl bromide gave methyl 2-methylpent-4-enoate. Reduction of this ester (or the

commercially available ethyl ester) with lithium aluminium hydride gave the alcohol. However, bromination with carbon tetrabromide gave bromoform as a by-product which could not be removed from the bromide, even after careful distillation. Conversion of the alcohol to the methanesulphonate ester and subsequent reaction with lithium bromide in acetone again gave the bromide but this time it was contaminated with the mesityl oxide produced by condensation of the acetone which again could not be removed by careful distillation. Attempted reaction of the crude bromide with sodium sulphite proved to be ineffective.

It was attempted to prepare 6-methylhept-5-en-2-sulphonyl chloride. Bromination of 6-methylhept-5-en-2-ol with bromine and triphenylphosphine gave 6-bromo-2-methylhept-2-ene, **14**,[219]



14

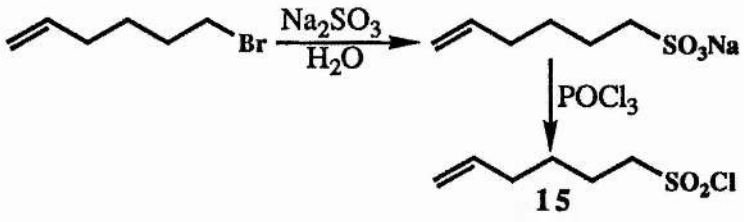
but repeated attempts to react this with sodium sulphite proved fruitless. Reaction of secondary bromides with sodium sulphite is inherently more difficult than that of primary bromides.

It is unfortunate that no substituted sulphonyl chlorides were prepared as it would have been interesting to observe the effect of substitution on cyclisation. The problem appeared to occur in the reaction between the bromide and sodium sulphite. Whilst this worked well with linear unsubstituted bromides, incorporation of an alkyl substituent β- to the bromine appeared to prevent reaction from occurring.

5.5 Cyclisation To Larger Rings.

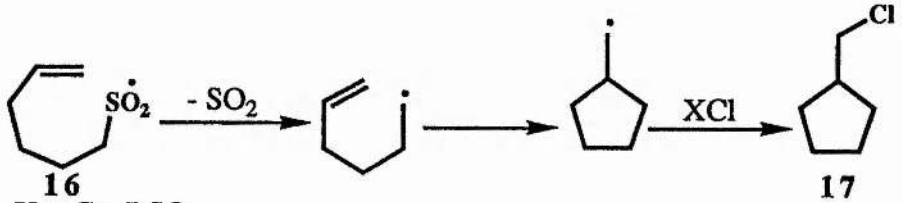
Whilst cyclisation to give seven-membered rings is inherently more difficult, cyclisation of the hexenesulphonyl radical, which was generated from hex-5-ene-1-sulphonyl chloride, was investigated. By an analogous synthesis to pentenesulphonyl chloride, hexenesulphonyl chloride, **15**, was prepared from 6-bromohex-1-ene using

sodium sulphite and phosphorus oxychloride.



15

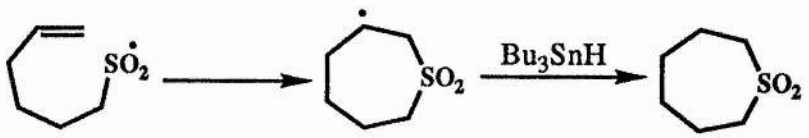
The hex-5-ene-1-sulphonyl radical, **16**, was generated in the cavity of an ESR spectrometer over the range (240-250 K), $a(2H_\alpha)$ 0.6, $a(2H_\beta)$ 2.1, $a(2H_\gamma)$ 0.6). Long range splittings were observed which corresponded to the γ-splittings, which have been observed before in long chain alkanesulphonyl radicals.[186] Use of the copper (II) chloride catalyst, which worked well for pentenesulphonyl chloride, proved unsuitable for hexenesulphonyl chloride. The relatively high temperatures required for the copper catalysed reaction to work, coupled with the fact that cyclisation is slow and difficult, gives ample time for α-scission of the sulphonyl radical to occur. This reaction generated mainly the hex-5-enyl radical which is well documented and cyclises in the *exo*-mode giving the cyclopentylmethyl radical.[220] Subsequent chlorine atom abstraction gives chloromethylcyclopentane, **17**, and this was the main product which was detected in the reaction mixture.



16
X = Cu, RSO_2

17

Using tri-*n*-butyltin hydride at a relatively low temperature (*ca.* 45 °C) gave the seven-membered ring product, thiepane-1,1-dioxide, **18**, in low yield.



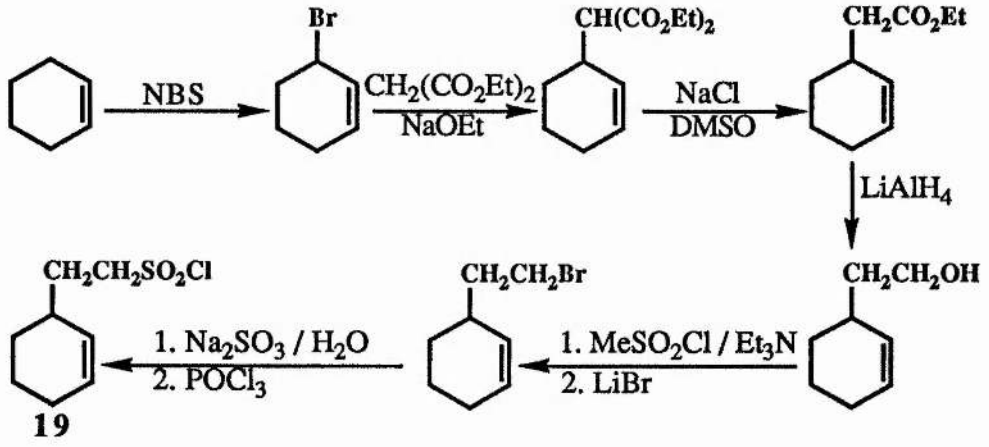
18

The product of *exo*-cyclisation, namely 2-methyltetrahydrothiopyran-1,1-dioxide was not detected. As the amount of *endo*- product was very low, the amount of *exo*-product, if it had formed, would probably have been below the detection limit. Reaction of hex-5-ene-1-sulphonyl chloride with tri-*n*-butyltin hydride in the presence of ultrasound also gave the seven membered ring thiepan-1,1-dioxide -identified in the mixture by GC/MS. The use of ultrasound to catalyse the cyclisation of hex-5-ene-1-sulphonyl chloride with copper (II) chloride had no effect and only unreacted starting material remained in the mixture.

In conclusion, the linear alkenesulphonyl radicals tend to cyclise almost exclusively in the *endo*-mode. This is not surprising as the long C–S bond enables steric problems in the transition state to be overcome, thus leading to the formation of the more stable cyclohexyl type secondary radical.

5.6 Bicyclisation And Regioselectivity.

Whilst is has been demonstrated that the cyclisation of sulphonyl radicals tends to be predominantly *endo*-, it has been possible to reverse the regiospecificity of the cyclisation such that it is exclusively *exo*, and this has been observed in the cyclisation of the cyclohexenylethanesulphonyl radical. This was generated from the corresponding sulphonyl chloride which was prepared as shown below.

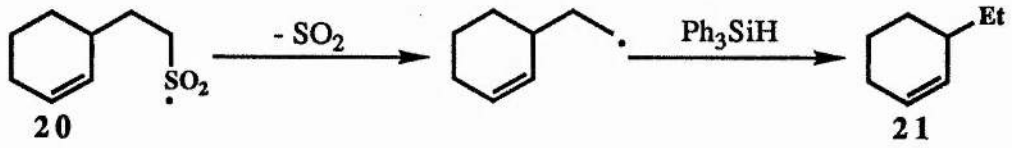


19

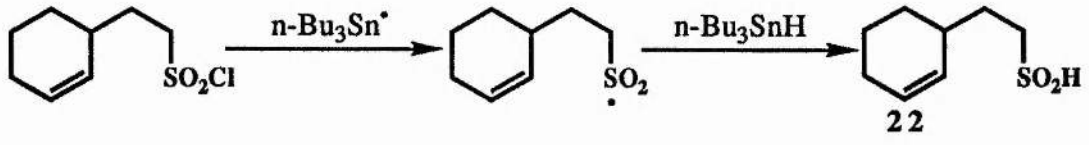
Bromination of cyclohexene with NBS gave 3-bromocyclohexene[36] which was then reacted with sodium ethoxide/diethyl malonate to give diethyl 2-cyclohexenyl malonate. Heating to 170 °C in DMSO in the presence of sodium chloride gave the mono-ester which was then reduced to the alcohol[221], brominated and converted to the sulphonyl chloride, **19**.

The cyclohexenylethanesulphonyl radical, **20**, was generated by chlorine abstraction from the corresponding sulphonyl chloride using photochemically generated trimethyltin radicals and the ESR spectrum of **20** was observed in the range (225-280 K), $a(2H_\alpha)$ 0.6, $a(2H_\beta)$ 1.7, $a(2H_\gamma)$ 0.6. No cyclised radical species were observed.

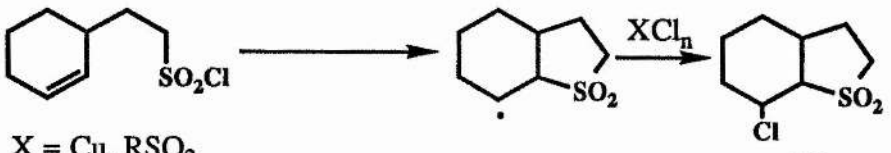
Cyclisation is somewhat hindered by the bulk of the cyclohexene ring and reaction with triphenylsilane under photolysis conditions at 170 °C proved to be unsuccessful. Apart from unreacted precursors (a problem also found in the pentenesulphonyl chloride reaction with triphenylsilane), the only product was ethyl cyclohexene, **21**, which is formed by α-scission of the first formed sulphonyl radical and then subsequent hydrogen abstraction.



The rate of cyclisation is slowed to such an extent that the use of tri-*n*-butyltin hydride and AIBN (a successful radical initiator system with pent-4-ene-1-sulphonyl chloride), proved to be unsuccessful. Before cyclisation can occur, hydrogen abstraction occurs from tin hydride to give cyclohexenylethanesulphinic acid, **22**, as the only observable product.



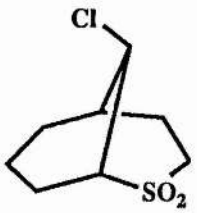
The low temperature reaction of tri-*n*-butyltin hydride with cyclohexenylethanesulphonyl chloride catalysed by ultrasound also failed to give any bicyclic products. However, the copper chloride-catalysed cyclisation did prove to be successful and the product was identified as 2-chloro-9-thiabicyclo[4.3.0]nonane-9,9-dioxide, **23**. This is the product of *exo*-cyclisation



X = Cu, RSO_2

23

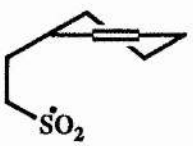
2D NMR (^1H–^{13}C correlation)was used to confirm this structure and eliminate the possibility of it being the product of *endo*- cyclisation, **24**.



24

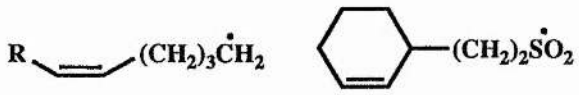
That cyclisation occurs exlusively in the *exo*-mode can be attributed to the following factors.

(i) In the half-chair ring conformation of the cyclohexenylethanesulphonyl radical, the ethanesulphonyl group will preferentially adopt a *quasi*-equatorial orientation.



Models indicate that in this conformation the radical centre is much better placed for five-membered ring formation.

(ii) It is known that radicals with *cis*-substituents on the terminal carbon of the double bond of the hex-5-enyl chain show an even greater preference for five-membered ring formation than hex-5-enyl itself, probably because of increased steric interaction in the transition state for six-membered ring formation between the *cis*-substituent and the hydrogens on C_β.[222] A similar effect would be exhibited in the transition state for six-membered ring formation from the *quasi*-axial (or *quasi*-equatorial) conformation of the cyclohexenylethanesulphonyl radical.



As can be seen above, the ring itself behaves as a *cis*-substituent.

5.7 Experimental.

Pent-4-ene-1-sulphonyl chloride.[202]

5-Bromopent-1-ene (10.0 g; 67.1 mmol) and sodium sulphite (10.3 g; 81.7 mmol) in water (35 cm^3) were refluxed overnight with rapid stirring. The solution was allowed to cool and then washed with diethyl ether. The aqueous layer was evaporated and the resulting white solid was dried under vacuum (130 °C/ 1 mmHg). Phosphorus oxychloride (57 g) was added to the dry solid and the mixture was heated, with stirring, to 120-140 °C. The solution was then cooled and poured carefully onto ice. The solution was then stirred for 20min to ensure all the phosphorus oxychloride was destroyed. Ether was added and the solution was extracted (x3). The combined ether layers were washed (water, sat.NaCl aq) and dried (Na_2SO_4 anhyd.). After evaporation, the crude sulphonyl chloride was distilled by kugelrohr (98 °C/ 1 mmHg; Lit.[202] 60-66 °C/ 0.3 mmHg) to yield a clear colourless liquid. Yield 5.0 g; 44%. δ_H 2.11-2.35 (4H, m), 3.69 (2H, t, $\underline{CH_2}SO_2Cl$), 5.07-5.16 (2H, m, CH_2), 5.69-5.82 (1H, m, CH); *m/z* 131 (1), 99 (1), 69 (12), 68 (35), 67 (100), 53 (21), 43 (11), 40 (25), 39 (40).

Reduction of pent-4-ene-1-sulphonyl chloride to pent-4-ene-1-sulphinic acid using tri-*n*-butyltin hydride.

Pent-4-ene-1-sulphonyl chloride (0.2 g; 1.19 mmol) was degassed and heated to 105 °C. Tri-*n*-butyltin hydride (0.32 cm^3; 1.19 mmol) was added very slowly, dropwise, and the mixture was photolysed for 5 hr. GC/MS on the black intractable tar produced showed no cyclised product nor the starting material. The mixture was diluted with ether and 2 M NaOH solution. The aqueous layer was removed and acidified with dil. HCl (pH paper) before re-extracting with ether (x2). The ether was dried (Na_2SO_4 anhyd.) and evaporated to give a white solid which proved to be the sulphinic acid. (Lit.[223]) δ_H 1.77 (2H,m, CH_2), 2.18 (2H, m, CH_2), 2.78 (2H, t, $\underline{CH_2}SO_2H$), 5.04 (2H, m, CH_2), 5.78 (1H, m, CH), 8.37 (1H, br s, $SO_2\underline{H}$).

Photolysis of pent-4-ene-1-sulphonyl chloride.

Pent-4-ene-1-sulphonyl chloride (0.2 g; 1.19 mmol) was degassed and photolysed at 170 °C for 1 hr. after which time it had gone black. Deuteriochloroform was added to the dark liquid and ^{1}H NMR showed it to be unreacted pent-4-ene-1-sulphonyl chloride.

Copper chloride catalyst.[203]

The copper chloride catalyst used was prepared from copper (II) chloride (0.175 g; Aldrich Gold label 99.999.%), triethylamine hydrochloride (0.250 g) and AIBN (0.150 g) in acetonitrile (5 cm^3).

Cyclisation of pent-4-ene-1-sulphonyl chloride using copper (II) chloride.

To pent-4-ene-1-sulphonyl chloride (0.3 g; 1.78 mmol), an equal volume of copper (II) chloride catalyst solution was added and the mixture degassed. The temperature was then raised to 170 °C, allowing the acetonitrile to boil off as the temperature increased. The mixture was maintained at 170 °C for 1.5 hr. The black viscous residue was purified by preparative TLC (x2) (eluent:- methylene chloride (40%): 40-60 °C petroleum ether (60%)). Yield 35.5 mg; 17%. The product was identified as 3-chlorotetrahydrothiopyran-1,1-dioxide. (Lit.[183]) δ_H 1.73 (H_4, d q), 2.07 (H_5, m), 2.20 ($H_{5'}$, d quint), 2.41 ($H_{4'}$, m), 2.93 (H_6, dt), 3.05 ($H_{6'}$, d q), 3.18 (H_2, q), 3.55($H_{2'}$, m),4.31 (H_3, tt). δ_C 21.72 (CH_2), 34.76 (CH_2), 50.32 (CH_2), 52.23 (CH), 59.52 (CH_2). *m/z* 168 (M^+, 1), 133 (34), 105 (9), 103 (31), 76 (53), 68 (45), 67 (100), 55 (44), 42 (45), 41 (98), 40 (47), 39 (63).

Cyclisation of pent-4-ene-1-sulphonyl chloride with tris (triphenylphosphine) ruthenium (II) chloride.

Pent-4-ene-1-sulphonyl chloride (0.2 g; 1.19 mmol), was heated to 170 °C and degassed. Tris(triphenylphosphine) ruthenium (II) chloride (0.12 g; 1.19 mmol) was

added and the mixture was heated at 170 °C for 2.5 hr. The mixture was purified by preparative TLC, (eluent: 40% methylene chloride: 60% 40-60 °C petroleum ether), to give 3-chlorotetrahydrothiopyran-1,1-dioxide as the product. Yield 29.7 mg; 15%.

Cyclisation of pent-4-ene-1-sulphonyl chloride with tri-*n*-butyltin hydride using AIBN as initiator.

A solution of pent-4-ene-1-sulphonyl chloride (0.2 g; 1.19 mmol) and tri-*n*-butyltin hydride (0.32 cm^3; 1.19 mmol) in dry benzene (2 cm^3) were degassed and heated to 80 °C. A solution of AIBN (0.04 g; 20% equiv.) in dry benzene (1 cm^3) was added slowly and the mixture was refluxed under nitrogen for 8 hr. After cooling, the mixture was analysed by GC/MS, and was shown to contain cyclised products; 3-chlorotetrahydrothiopyran-1,1-dioxide (74% rel.) and tetrahydrothiopyran-1,1-dioxide (26% rel.).

When this experiment was repeated at 45-50 °C over 24 hr., subsequent analysis of the mixture showed that the non-chlorinated sulphone became the major product; 3-chlorotetrahydrothiopyran-1,1-dioxide (20% rel.) and tetrahydrothiopyran-1,1-dioxide (80% rel.).

Reduction of 3-chlorotetrahydrothiopyran-1,1-dioxide using tri-*n*-butyltin hydride.

To a degassed solution of 3-chlorotetrahydrothiopyran-1,1-dioxide (24.3 mg; 0.144 mmol) in dry benzene (0.5 cm^3) was added tri-*n*-butyltin hydride (42.7 µl; 0.159 mmol) and the mixture was refluxed under nitrogen for 4 hr. Analysis of the reaction mixture by GC/MS showed the product to be tetrahydrothiopyran-1,1-dioxide. The mixture was purified by preparative TLC using 40% methylene chloride:60% 40-60 °C petroleum ether as the eluent, (see triphenylsilane reaction for spectra).

Cyclisation of pent-4-ene-1-sulphonyl chloride with tri-*n*-butyltin hydride using ultrasound as initiator.

To a degassed solution of pent-4-ene-1-sulphonyl chloride in dry benzene (0.5 cm^3) was slowly added tri-*n*-butyltin hydride (0.32 cm^3; 1.19 mmol). No reaction was observable at this stage. The sample tube was then suspended in an ultrasonic bath at ambient temperature and subjected to ultrasonification for 1.75 hr. A rapid effervescence was observed as soon as the ultrasonic bath was switched on. Analysis of the mixture by GC/MS showed that cyclisation had proceeded in a manner analogous to the low temperature tri-*n*-butyltin hydride/AIBN reaction to give tetrahydrothiopyran-1,1-dioxide as the only observable product.

Removal of tin residues.

The mixture contaminated with tri-*n*-butyltin hydride was evaporated and carbon tetrachloride (20 cm^3; for a mixture containing about 1 g tin hydride) added. After reflux for 1.5 hr. the solution was cooled, evaporated and a saturated solution of iodine in methylene chloride (50 cm^3) and a saturated aqueous solution of potassium fluoride (50 cm^3) were added. After stirring the mixture overnight it had become pale yellow. The solution was then filtered through HiFlo Supercel, the methylene chloride layer was removed and the aqueous was further extracted (x3). The combined methylene chloride layers were washed with 2 M sodium thiosulphate solution (50 cm^3), water (50 cm^3), and saturated sodium chloride solution, dried ($MgSO_4$ anhyd.) and evaporated.

Cyclisation of pent-4-ene-1-sulphonyl chloride with triphenylsilane.

Pent-4-ene-1-sulphonyl chloride (0.3 g; 1.78 mmol) was heated to 150 °C and degassed. Triphenylsilane (0.46 g; 1.78 mmol) was added and the mixture stirred. The temperature was raised to 170 °C whilst the sample was photolysed by UV light from a 250 W medium pressure Hg arc lamp for 30 min. Not all of the sulphonyl chloride had

reacted during the experiment so a yield was not recorded. The products obtained were 3-chlorotetrahydrothiopyran-1,1-dioxide (78% rel.) and tetrahydrothiopyran-1,1-dioxide (8% rel.). δ_H ($C_5H_{10}SO_2$) 1.65 (2H, m, H_4), 2.12 (4H, m, H_3), 3.00 (4H, br t, H_2). (Lit.[224]) δ_C ($C_5H_{10}SO_2$) 23.91 (CH_2), 24.29 (CH_2), 52.21 (CH_2). *m/z* 134 (M^+, 19), 133 (2), 117 (4), 106 (7), 71 (4), 69 (54), 55 (30), 42 (56), 41 (100), 39 (22). When the reaction was carried out at 75 °C, 2-chloromethyltetrahydrothiophene-1,1-dioxide was identified in the mixture. The five and six membered ring products could not be separated by preparative TLC, but the NMR of the six-membered product did reveal some of the five-membered product to be present. Those peaks not overlapped were (Lit.[225]) δ_H 3.95, 3.65 (2H, dd, CH_2Cl). δ_C 19.91 (CH_2), 28.13 (CH_2), 40.68 (CH_2), 52.10 (CH_2Cl), 61.81 (CH). *m/z* 133 (*M*-Cl, 18), 122 (11), 120 (14), 69 (48), 67 (22), 41 (100), 39 (34).

5-Chloropentene was observed in the reaction mixture by GC/MS, *m/z* 104 (M^+, 6), 69 (7), 68 (35), 67 (52), 55 (84), 41 (100), 39 (80).

9-Trimethylstannyl-9,10-dihydroanthracene.[209]

9,10-Dihydroanthracene (4.0 g; 22.2 mmol) in dry ether (56 cm^3) was cooled to 0 °C under N_2. A solution containing 33.3 mmol of *n*-butyl lithium (13.3 cm^3 of a 2.5 M solution in hexane) was added dropwise, the solution turning from colourless to black. The mixture was stirred at 0 °C for 1 hr. then at room temperature overnight. A solution of trimethyl tin chloride (6.66 g; 33.3 mmol) in dry ether (23 cm^3) was added dropwise to the dark solution of lithium anthracenide at 0 °C under N_2. and then stirred at room temperature for 1 hr. The solution was then poured onto water (50 cm^3) and the ether extracted. The aqueous was re-extracted and the combined ether layers were washed (sat. NaCl aq., water), dried (Na_2SO_4 anhyd.) and evaporated to dryness before pumping dry at 1 mmHg for 1 hr. The yellow product was dissolved in chloroform (12 cm^3) to dissolve the tin compound whilst leaving behind any unreacted anthracene. The solution was filtered, evaporated under reduced pressure and pumped dry (1 mmHg) to leave a bright yellow solid. The solid was recrystallised twice from

ethanol and dried (70 °C/ 1 mmHg). M.pt. 98-100 °C. (Lit.[209] 103 °C). Yield 2.60 g; 34%. *m/z* 344 (M^+, 1), 329 (1), 299 (1), 179 (52), 178 (100), 165 (15), 152 (7), 135 (5), 120 (3), 88 (14), 76 (13).

Cyclisation of pent-4-ene-1-sulphonyl chloride with 9-trimethylstannyl-9,10-dihydroanthracene.

To pent-4-ene-1-sulphonyl chloride (0.3 g; 1.79 mmol) was added 9-trimethylstannyl-9,10-dihydroanthracene (0.6 g; 1.79 mmol). The mixture was heated to 170 °C, degassed and photolysed for 2 hr. Subsequent analysis by GC/MS showed cyclised products to have formed in the ratio of 3-chlorotetrahydrothiopyran-1,1-dioxide (91% rel.) and 2-chloromethyltetrahydrothiophene-1,1-dioxide (9% rel.).

Cyclisation of pent-4-ene-1-sulphonyl chloride with hexa-*n*-butylditin.

Pent-4-ene-1-sulphonyl chloride (0.2 g; 1.19 mmol) in dry benzene (2 cm^3) was degassed and stirred at 40 °C under N_2. AIBN (0.04 g; 20% equiv.) was added and a solution of hexa-*n*-butylditin (0.12 cm^3) in dry benzene (2 cm^3) was added dropwise. The mixture was stirred at 40 °C for 5 hr after which it was analysed by GC/MS. Both products of *endo*- and *exo*-cyclisation were detected in the ratio 8:1 respectively.

Dihydrothiopyran-1,1-dioxide.

To 3-chlorotetrahydrothiopyran-1,1-dioxide (28.2 mg; 0.168 mmol) in dry benzene (0.5 cm^3) under N_2 was added DBU (40.9 mg; 0.269 mmol) dropwise with stirring. The mixture was then heated to reflux for 1.5 hr. before cooling and diluting with dil.HCl. The mixture was then extracted with methylene chloride (x3) and the combined organics were washed (sat. NaCl aq.), dried ($MgSO_4$ anhyd.) and evaporated, to give the crude product. δ_H 2.63 (2H, m, CH_2), 2.97 (2H, t, CH_2), 3.52 (2H, m, CH_2), 5.51-5.76 (2H, m, CH=CH). δ_C 25.80 (CH_2), 47.43 (CH_2), 50.79 (CH_2), 119.42 (CH), 126.83 (CH). *m/z* 132 (M^+, 1), 68 (24), 67 (100), 53 (22), 41

(24), 39 (34).

Attempted cyclisation of pent-4-ene-1-sulphonyl chloride using dibenzoyl peroxide.

A mixture of pent-4-ene-1-sulphonyl chloride (0.1 g; 0.595 mmol) and dibenzoyl peroxide (7.24 mg; 5% equiv.) were degassed and heated to 160-170 °C for 1 hr. Analysis of the mixture by GC/MS showed that no reaction had occurred.

Attempted cyclisation of pent-4-ene-1-sulphonyl chloride using triethylsilane, *tert*-dodecanethiol and dilauroyl peroxide.

A degassed solution of pent-4-ene-1-sulphonyl chloride (0.84 g; 5.0 mmol), triethylsilane (1.16 g; 10.0 mmol), dilauroyl peroxide (0.04 g; 2% equiv.) and *tert*-dodecanethiol (0.02 g; 2% equiv.) in cyclohexane (5 cm^3) was refluxed under nitrogen for 11 hr. The mixture was then cooled and diluted to 15 cm^3 with cyclohexane. The solution was then washed with water and 6 M NaOH solution (20 cm^3), extracted, dried ($MgSO_4$ anhyd.) and evaporated. Analysis of the residue by ^1H NMR and GC/MS showed that the sulphonyl chloride had not cyclised.

***iso*-Propyl pent-4-ene-1-sulphonate.**

To a solution of *iso*-propanol (0.5 g; 8.3 mmol) and triethylamine (0.85 g; 8.4 mmol) in dry methylene chloride (10 cm^3) at 0 °C under nitrogen was added pent-4-ene-1-sulphonyl chloride (1.53 g; 9.1 mmol) dropwise. After stirring at 0 °C for 1 hr. the mixture was washed (water, dil. HCl, water, Sat NaCl aq.), dried (Na_2SO_4 anhyd.) and evaporated. δ_H 1.49 (6H, d, CH_3), 1.90-2.43 (5H, m), 3.09 (2H, br t, $\underline{CH_2}SO_2$), 4.67-5.33 (2H, m, CH_2), 5.40-6.15 (1H, m, CH). IR υ cm^{-1}, 2935 (sp^2 C–H), 1350 (asym. O=S=O), 1175 (sym. O=S=O).

Attempted cyclisation of *iso*-propyl pent-4-ene-1-sulphonate with tri-*n*-butyltin hydride under photolysis conditions.

To *iso*-propyl pent-4-ene-1-sulphonate (0.2 g; 1.04 mmol) was added tri-*n*-butyltin hydride (0.28 cm^3; 1.04 mmol). The mixture was photolysed for 3.5 hr. at 170 °C. Analysis of the mixture only revealed the presence of starting material. In order to determine whether any of the ester had been reduced to the sulphinic acid the reaction mixture was diluted with ether and washed with 2 M NaOH solution. The aqueous layer was separated and acidified with conc. hydrochloric acid. The acidified aqueous layer was extracted with ether (x2), dried (Na_2SO_4 anhyd.) and evaporated. The residue which remained was not pent-4-ene-1-sulphinic acid

Attempted cyclisation of *iso*-propyl pent-4-ene-1-sulphonate with tri-*n*-butyltin hydride using AIBN as initiator.

To a degassed solution of *iso*-propyl pent-4-ene-1-sulphonate (0.5 g; 2.6 mmol) and AIBN (0.043 g; 10% equiv.) in dry toluene (5 cm^3) heated to 100 °C under nitrogen was added tri-*n*-butyltin hydride (0.86 cm^3; 3.2 mmol) over 1 hr. The mixture was maintained at 100 °C for 5 hr. Analysis of the mixture by GC/MS only revealed the starting materials.

Attempted cyclisation of *iso*-propyl pent-4-ene-1-sulphonate with tri-*n*-butyltin hydride using dibenzoyl peroxide as initiator.

To a degassed mixture of *iso*-propyl pent-4-ene-1-sulphonate (0.2 g; 1.0 mmol) and dibenzoyl peroxide (0.05 g; 20% equiv.) at 100 °C was added tri-*n*-butytin hydride (0.29 cm^3; 1.04 mmol) over a period of 3 hr. After heating for a total of 5.5 hr. the mixture was analysed by GC/MS but only starting materials were present.

Ethyl 2,2-dimethylpent-4-enoate.

To a solution of di-*iso*-propylamine (15.18 g; 0.150 mol) in dry THF (150 cm^3) at -78 °C under N_2 was added a solution containing 0.150 mol of *n*-butyl lithium (60 cm^3 of a 2.5 M solution in hexane) dropwise. The solution was then stirred at room temperature for 15 min. before re-cooling to -78 °C. Ethyl *iso*-butyrate (17.25 g; 0.150 mol) was then added dropwise and the mixture was stirred at -78 °C for 30 min. To this cooled mixture, a solution of allyl bromide (18.5 g; 0.153 mol) in HMPT (25 cm^3) was added dropwise and the resultant solution was then allowed to slowly reach room temperature, whilst stirring overnight. The solution was then diluted with water and the THF layer removed. The aqueous layer was further extracted with 40-60 °C petroleum ether (x2). The combined organic layers were then washed (water, dil, HCl, sat. $NaHCO_3$ aq.), dried (Na_2SO_4), evaporated and distilled by kugelrohr (74 °C/ 14 mmHg; Lit.[215] 61 °C/ 17 mmHg). Yield 18.9 g; 81%. δ_H 1.18 (6H, s, CH_3), 1.24 (3H, t, $CH_2\underline{CH_3}$), 2.30 (2H, d, CH_2), 4.11 (2H, q, $\underline{CH_2}CH_3$), 4.79-5.26 (2H, m, CH_2), 5.39-6.17 (1H, m, CH).

2,2-Dimethylpent-4-en-1-ol.

To a solution of lithium aluminium hydride (2.2 g; 58.0 mmol) in dry ether (250 cm^3) under N_2 was added dropwise, with stirring, ethyl 2,2-dimethylpent-4-enoate (17.5 g; 0.111 mol) in dry ether (60 cm^3) after which the mixture was refluxed for 1 hr then allowed to cool, before stirring overnight at room temperature. The excess reducing agent was decomposed by careful addition of water. The ether layer was removed and the etherate complex remaining was broken up with dil. HCl. The aqueous layer was further extracted with ether (x3). The combined ether layers were washed (sat. NaCl aq.), evaporated and distilled by kugelrohr (80 °C/ 14 mmHg; Lit.[215] 62 °C/ 15 mmHg). Yield 11.4 g; 90%. (Lit.[218]) δ_H 0.87 (6H, s, CH_3), 1.80 (1H, s, OH), 2.02 (2H, d, CH_2), 3.33 (2H, s, $\underline{CH_2}OH$), 4.79-5.27 (2H, m, CH_2), 5.50-6.27 (1H ,m, CH).

5-Bromo-4,4-dimethylpent-1-ene.[215]

A solution of 2,2-dimethylpent-4-en-1-ol (9.0 g; 78.8 mmol) and triphenyl phosphine (21.15 g; 80.6 mmol) in methylene chloride (45 cm^3), was cooled to 0 °C under N_2. Carbon tetrabromide (29.7 g; 89.6 mmol) was added in small portions (exothermic reaction) and the mixture was stirred overnight at room temperature.The solvent was carefully evaporated off, and the residue was distilled through a column of helices (65 °C/ 14 mmHg). Unfortunately, it proved impossible to remove all the bromoform which had formed as a by-product of the reaction, because their boiling points were too similar. (Lit.[215]) δ_H 1.03 (6H, s, CH_3), 2.13 (2H, d, CH_2), 3.29 (2H, s, $\underline{CH_2}Br$), 4.89-5.37 (2H, m, CH_2), 5.49-6.26 (1H, m, CH).

Methyl 2-methylpent-4-enoate.

To di-*iso*-propylamine (15.18 g; 0.150 mol) in THF (150 cm^3) at -78 °C under N_2 was added dropwise a solution containing 0.150 mol of *n*-butyl lithium (60 cm^3 of a 2.5 M solution in hexane). It was then stirred at room temperature for 15 min. before re-cooling to -78 °C. Methyl propionate (13.1 g; 0.150 mol) was added dropwise and the mixture stirred for 30 min. at -78 °C. Allyl bromide (18.5 g; 0.153 mol) in HMPT (25 cm^3) was added dropwise and the mixture allowed to stir overnight at room temperature. The mixture was then diluted with water and extracted. The aqueous layer was re-extracted with 40-60 °C petroleum ether (x2). The combined organic layers were washed (water, dil. HCl, sat. $NaHCO_3$ aq.), dried (Na_2SO_4 anhyd.), evaporated and distilled by kugelrohr (67 °C/ 14 mmHg; Lit.[226] 137.5 °C/ 760 mmHg). Yield 8.86 g; 42%. (Lit.[226]) δ_H 1.01 (3H, d, CH_3), 2.06-2.80 (3H, m, CH, CH_2), 3.75 (3H, s, CH_3-ester), 4.99-5.44 (2H, m, CH_2), 5.62-6.19 (1H, m, CH).

2-Methylpent-4-en-1-ol.

To a stirred solution of lithium aluminium hydride (4.0 g; 0.105 mol) in dry ether (300 cm^3) under N_2 was added dropwise ethyl 2-methylpent-4-enoate (20.0 g; 0.138 mol) in dry ether (75 cm^3). The mixture was stirred overnight at room

temperature and then refluxed for 1 hr. After cooling, the excess lithium aluminium hydride was carefully decomposed with water and the ether layer was removed. The aqueous etherate was broken up with conc. HCl and re-extracted with ether (x3). The combined ether layers were washed (sat. NaCl aq.), dried (Na_2SO_4 anhyd.) evaporated and distilled by kugelrohr (53-55 °C/ 14 mmHg; Lit.[183] 53-58 °C/ 14 mmHg). Yield 10.3 g; 75%. (Lit.[183]) δ_H 0.91 (3H, d, CH_3), 1.39-2.39 (3H, m, CH, CH_2), 3.47 (2H, d, $\underline{CH_2}OH$), 4.78-5.24 (2H, m, CH_2), 5.43-6.23 (1H, m, CH).

6-Bromo-2-methylhept-2-ene.[219]

To a cooled suspension of triphenylphosphine (20.95 g; 80 mmol) in acetonitrile (350 cm^3) was added a solution of bromine (12.8 g; 0.16 mol) in acetonitrile (70 cm^3). Pyridine (6.5 cm^3; 80 mmol) was added and the mixture was stirred at room temperature for 15 min. 6-Methylhept-5-en-2-ol (10.0 g; 78 mmol) in acetonitrile (70 cm^3) was added dropwise over 20-25 min., after which it was stirred for a further 1 hr. The acetonitrile was then carefully evaporated to yield a white solid. Ethyl acetate (75 cm^3) and water (75 cm^3) were added and the mixture was extracted (x2). The ethyl acetate was washed (sat. NaCl aq.), dried ($MgSO_4$ anhyd.) and evaporated. Some solid was still present, so diethyl ether was added and the solid was filtered off. The ether layer was evaporated and distilled by kugelrohr (93 °C/ 14 mmHg; Lit.[219] 32-38 °C/ 0.75 mmHg). Yield 6.0 g; 40.2%. (Lit.[219]) δ_H 1.78 (6H, s, CH_3), 1.85 (3H, d, CH_3), 1.01-2.41 (4H, m), 4.13 (1H, m, $\underline{CH}Br$), 5.09 (1H, br t, CH=C).

Hex-5-ene-1-sulphonyl chloride.

6-Bromohex-1-ene (4.75 g; 29.1 mmol) and sodium sulphite (4.41 g; 34.99 mmol) were refluxed overnight in water (15 cm^3). The solution was then cooled and washed with ether, after which the aqueous layer was evaporated to dryness to give hex-5-ene-1-sulphinic acid sodium salt as a white solid. The solid was dried (130 °C/ 1 mmHg) before cooling to room temperature and carefully adding phosphorus

oxychloride (25 g). The mixture was then heated to 120-140 °C for 3.5 hr. before cooling and pouring onto ice. It was stirred in ice-water for 15 min. before extracting with ether (x2). The combined ether layers were washed (water, sat. NaCl aq.), dried (Na_2SO_4 anhyd.), evaporated and distilled by kugelrohr (121 °C/ 1 mmHg). Yield 2.45 g; 46%. δ_H 1.62 (2H, m, CH_2), 1.97-2.20 (4H, m, CH_2), 3.79 (2H, t, $\underline{CH_2}SO_2Cl$), 5.06 (2H, m, CH_2), 5.70-5.86 (1H, m, CH). δ_C 23.68 (CH_2), 26.64 (CH_2), 32.87 (CH_2), 65.27 (CH_2SO_2Cl), 115.86 (CH_2), 137.09 (CH).

Attempted cyclisation of hex-5-ene-1-sulphonyl chloride with copper (II) chloride.

Hex-5-ene-1-sulphonyl chloride (0.3 g; 1.64 mmol) and an equal volume of copper (II) chloride catalyst were heated (allowing the acetonitrile to evaporate off) to 160 °C for 1.5 hr. The reaction mixture was analysed by GC/MS but neither chlorinated or non-chlorinated products of cyclisation were detected. The major product however appeared to be chloromethylcyclopentane which would be formed if the initial sulphonyl radical lost SO_2 to form the hex-5-enyl radical which is known to cyclise in the *exo*-mode to give the methylcyclopentyl radical which subsequently abstracts chlorine. *m/z* ($C_5H_{11}Cl$) 118 (M^+, 3), 92 (4), 90 (6), 83 (7), 82 (15), 69 (31), 67 (42), 55 (70), 41 (100).

Cyclisation of hex-5-ene-1-sulphonyl chloride with tri-*n*-butyltin hydride using AIBN as initiator.

Hex-5-ene-1-sulphonyl chloride (0.2 g; 1.09 mmol) in dry benzene (1 cm^3) was degassed, and AIBN (0.04 g; 20% equiv.) added. The mixture was heated to 50 °C under N_2 and tri-*n*-butyltin hydride (0.35 cm^3; 1.30 mmol) in dry benzene (1 cm^3) was added dropwise and the mixture was stirred for 11 hr. Analysis of the mixture by GC/MS indicated that the sole product of cyclisation was thiepane-1,1-dioxide. (Lit.[227]) *m/z* 148 (M^+, 4), 131 (4), 120 (5), 83 (24), 67 (10), 56 (60), 55 (100), 41 (87), 39 (32).

Cyclisation of hex-5-ene-1-sulphonyl chloride with tri-*n*-butyltin hydride using ultrasound as initiator.

To a degassed solution of hex-5-ene-1-sulphonyl chloride (0.2 g; 1.09 mmol) in dry benzene (0.5 cm^3) was added tri-*n*-butytin hydride (0.3 cm^3; 1.09 mmol). The sample tube was suspended in an ultrasonic bath at ambient temperature and subjected to ultrasonification for 2.75 hr. No reaction was observed during the experiment, but analysis of the mixture by GC/MS showed the presence of thiepane-1,1-dioxide in low yield.

Attempted cyclisation of hex-5-ene-1-sulphonyl chloride with copper (II) chloride using ultrasound as initiator.

To hex-5-ene-1-sulphonyl chloride (0.2 g; 1.09 mmol) was added an equal volume of copper chloride catalyst solution. After degassing, the sample tube was suspended in an ultrasonic bath and subjected to ultrasonification for 6 hr. Analysis of the reaction mixture by GC/MS showed that no reaction had occurred, and that only the precursors were present.

3-Bromocyclohexene.[36]

A solution of *N*-bromosuccinimide (39.4 g; 0.221 mol), cyclohexene (49.7 g; 0.605 mol) and benzoyl peroxide (0.5 g; 2.06 mmol) in carbon tetrachloride (150 cm^3) was refluxed for 2.5 hr.(until starch-iodide paper remained white, *i.e.* no NBS or peroxide (both oxidants) remained). The mixture was then cooled and the succinimide was filtered off. After distillation of the carbon tetrachloride at atmospheric pressure the residue was distilled on a kugelrohr (89 °C/ 14 mmHg; Lit.[36] 66-67 °C/ 20 mmHg) to give pure 3-bromocyclohexene. Yield 25.4 g; 71%. δ_H 1.08-2.58 (6H, m, H_4, H_5, H_6), 4.68-5.10 (1H, m, H_1), 5.58-6.14 (2H, m, H_2, H_3).

Diethyl cyclohex-2-enylmalonate.[221]

To a cooled solution of sodium (8.29 g; 0.361 mol) in absolute ethanol (290 cm^3),under N_2,was added diethyl malonate (48.9 g; 0.370 mol) dropwise with stirring. The reaction mixture was cooled to 0 °C and 3-bromocyclohexene (51.5 g; 0.320 mol) was added slowly over about 45 min. It was then allowed to stand overnight before filtering off the white solid precipitate. The filtrate was evaporated under vacuo and water and ethyl acetate were added to the residue and extracted. The aqueous was further extracted (x2) after which the combined ethyl acetate layers were washed (sat.NaCl aq., water, sat.NaCl aq.), dried (Na_2SO_4 anhyd.), evaporated under reduced pressure and distilled by kugelrohr (165 °C/ 1 mmHg; Lit.[221] 124-127 °C/ 18 mmHg). Yield 49.7 g; 65%. (Lit.[221]) δ_H 1.22 (6H, t, $CH_2\underline{CH_3}$), 1.42-2.19 (7H, m, H_4, H_5, H_6, H_1), 2.58-3.04 (1H, m, CH-methine), 4.18 (4H, q, $\underline{CH_2}CH_3$), 5.27-5.89 (2H, m, H_2, H_3).

Ethyl cyclohex-2-enylacetate.[221]

Diethyl cyclohex-2-enylmalonate (48.0 g; 0.200 mol), sodium chloride (15.1 g; 0.258 mol) and water (9.22 cm^3) were heated to 170 °C in DMSO overnight. The solution was cooled and diluted with water after which it was extracted with ether (x3) and ethyl acetate (x2). The combined organic layers were washed with large portions of water (x3) to remove the DMSO, dried (Na_2SO_4 anhyd.), evaporated under reduced pressure and distilled by kugelrohr (127 °C/ 1 mmHg; Lit.[221] 84-89 °C/ 18 mmHg). Yield 26.6 g; 79%. (Lit.[221]) δ_H 1.22 (3H, t, $CH_2\underline{CH_3}$), 1.44-2.11 (9H, m, H_4, H_5, H_6, H_1, CH_2COO), 4.16 (2H, q, $\underline{CH_2}CH_3$), 5.43-5.91 (2H, m, H_2, H_3).

(2-Cyclohex-2-en-1-yl)ethanol.[221]

Ethyl cyclohex-2-enylacetate (25.0 g; 0.15 mol) was added dropwise to a suspension of lithium aluminium hydride (4.26 g; 0.11 mol) in dry ether (140 cm^3) at 0 °C under N_2. The mixture was stirred overnight, then refluxed for 2 hr. After cooling, the excess lithium aluminium hydride was carefully decomposed with water.

The ether was extracted and the aqueous etherate was broken up with HCl. The aqueous was re-extracted (x4) and the combined ether layers were washed (sat. NaCl aq.) dried (Na_2SO_4 anhyd.), evaporated under reduced pressure and distilled by kugelrohr (117 °C/ 1 mmHg; Lit.[221] 82-86 °C/ 12 mmHg). Yield 12.2 g; 64%. (Lit.[221]) δ_H 0.94-2.48 (10H, m, H_4, H_5, H_6, H_1, CH_2, OH), 3.68 (2H, t, $\underline{CH_2}OH$), 5.36-5.90 (2H, m, H_2, H_3).

3-(2-Bromoethyl)cyclohexene.

To the alcohol (6.0 g; 47.6 mmol) and triethylamine (4.82 g; 47.6 mmol) in methylene chloride (40 cm^3) at 0 °C under N_2, was added dropwise methanesulphonyl chloride (5.98 g; 52.37 mmol).The solution was stirred for 45 min. and was then washed (water, dil HCl, water, sat.NaCl aq.), dried (Na_2SO_4 anhyd.) and evaporated under reduced pressure. The crude mesylate was then added dropwise to a solution of lithium bromide (8.27 g; 95.22 mmol) in Analar acetone (90 cm^3). It was then stirred at room temperature for 30 min. before refluxing overnight ($CaCl_2$ guard tube).The solution was then allowed to cool before filtering. The filtrate was evaporated under reduced pressure before water and ether were added. The ether was extracted and the aqueous layer re-extracted (x3). The combined ether layers were washed (water), dried (Na_2SO_4 anhyd.), evaporated under reduced pressure and distilled by kugelrohr (95 °C/ 1 mmHg; Lit.[228] 50-70 °C/ 0.2 mmHg). Yield 6.8 g; 76%. δ_H 0.86 (9H, m, H_4, H_5, H_6, H_1, CH_2), 3.50 (2H, t, $\underline{CH_2}Br$), 5.36-5.98 (2H, m, H_2, H_3).

2-(Cyclohex-2-en-1-yl)ethanesulphonyl chloride.

3-(2-Bromoethyl)cyclohexene (6.0 g; 31.7 mmol) and sodium sulphite (5.07 g; 40.2 mmol)were refluxed overnight in water (16.1 cm^3).The solution was then cooled and washed with ether. The aqueous layer was then evaporated under reduced pressure to yield the solid white cyclohexenylethanesulphinic acid sodium salt, which was then dried (135 °C/ 1 mmHg). The solid was then cooled and phosphorus oxychloride (50 g) was carefully added and the mixture heated to 120-140 °C for 2 hr. The mixture

was then cooled and poured onto ice and the solution stirred for 15 min. The aqueous was then extracted with ether (x3) and the combined ether layers dried (Na_2SO_4 anhyd.), evaporated under reduced pressure and distilled by kugelrohr (169 °C/ 1 mmHg). Yield 1.65 g; 25%. δ_H 1.28 (1H, m), 1.57 (1H, m), 1.78 (2H, m, CH_2), 1.91-2.20 (4H, m, CH_2), 2.34 (1H, m), 3.71 (2H, t, $\underline{CH_2}SO_2Cl$), 5.44-5.85 (2H, m, CH=CH). δ_C 21.01 (CH_2), 25.00 (CH_2), 28.28 (CH_2), 30.06 (CH_2), 33.47 (CH), 63.40 (CH_2), 128.70 (CH), 129.62 (CH).

Attempted cyclisation of cyclohexenylethanesulphonyl chloride with triphenylsilane.

Cyclohexenylethanesulphonyl chloride (0.2 g; 0.959 mmol), was heated to 170 °C and degassed. Triphenylsilane (0.25 g; 0.959 mmol) was added and the mixture was photolysed at 170 °C for 2 hr. Analysis of the residue by GC/MS indicated that the mixture contained some unreacted sulphonyl chloride, but the major product was 3-ethylcyclohexene. *m/z* 110 (M^+, 19), 95 (14), 82 (15), 81 (100), 79 (32), 77 (14), 67 (24), 51 (7), 39 (16).

Reduction of cyclohexenylethanesulphonyl chloride to cyclohexenyl-ethanesulphinic acid using tri-*n*-butyltin hydride.

To a degassed solution of cyclohexenylethanesulphonyl chloride (0.2 g; 0.96 mmol) and AIBN (0.032 g; 20% equiv.) in dry benzene (1 cm^3) was added dropwise a solution of tri-*n*-butyltin hydride (0.26 cm^3; 0.96 mmol) in benzene (1 cm^3). The mixture was heated at 40 °C under nitrogen for 24 hr. Analysis of the mixture by GC/MS showed neither cyclised product or starting material were present. The reaction mixture was diluted with ether and washed with 2 M NaOH solution. The aqueous layer was removed and acidified using conc. hydrochloric acid. The acidified aqueous layer was extracted with ether (x2), dried ($MgSO_4$ anhyd.) and evaporated to give cyclohexenylethanesulphinic acid. δ_H 1.00-2.49 (9H, m), 2.80 (2H, br t, $\underline{CH_2}SO_2$), 5.26-5.92 (2H, m, CH), 8.28 (1H, br s, SO_2H).

Attempted cyclisation of cyclohexenylethanesulphonyl chloride with tri-*n*-butyltin hydride using ultrasound as initiator.

To a degassed solution of cyclohexenylethanesulphonyl chloride (0.2 g; 0.96 mmol) in dry benzene (0.5 cm^3) was added tri-*n*-butyltin hydride (0.26 cm^3; 0.96 mmol). No visible reaction was observed. The sample was suspended in an ultrasonic bath at ambient temperature and subjected to ultrasonification for 2.75 hr. Effervescence was observed when the ultrasonic bath was switched on which suggested a reaction had commenced. Analysis by GC/MS failed to show any cyclised material or starting sulphonyl chloride and so it can be assumed that the sulphonyl chloride has been reduced to the sulphinic acid.

2-Chloro-9-thiabicyclo[4.3.0]nonane-9,9-dioxide.

A mixture of cyclohexenylethanesulphonyl chloride (0.2 g; 0.96 mmol) and copper (II) chloride catalyst solution (equal volume), was degassed and heated to 110 °C (allowing the acetonitrile to evaporate off). After 3 hr. at 140 °C, the sample had gone black. The residue was purified by preparative TLC, (40% methylene chloride:60% 40-60 °C petroleum ether). Yield 31.2 mg; 16%. δ_H 1.48-1.90 (5H, m, H_3, H_4, H_4', H_5, H_5'), 1.93-2.28 (2H, m, H_7, H_7'), 2.28-2.45 (1H, m, H_3'), 2.78 (1H, m, H_6), 3.24 (2H, m, H_8, H_8'), 3.43 (1H, m, H_1), 4.55 (1H, q, CHCl). δ_C 19.09 (C_4), 25.76 (C_7), 26.36 (C_5), 31.82 (C_3), 35.00 (C_6), 51.36 (C_8), 53.64 (C_2), 67.27 (C_1). *m/z* 173 (*M*-Cl, 2), 143 (4), 142 (6), 116 (13), 107 (38), 93 (34), 91 (16), 81 (62), 80 (46), 79 (100), 77 (27), 67 (49), 65 (15), 53 (22), 41 (30), 39 (33).

Part Three

Tellurium Centred Free Radicals

Chapter Six

Introduction To Organotellurium Compounds.

6.1 Organotellurium Compounds.

Dialkyltellurides, R_2Te, have found use, together with elemental mercury and dimethylcadmium, as precursors in the metal-organic vapour phase epitaxy (MOVPE) of cadmium mercury telluride (CMT). In preparing CMT by MOVPE, the decomposition temperature of the tellurium alkyl is crucial in determining the minimum temperature at which epitaxial pyrolytic growth can occur. A low growth temperature is desirable as it reduces the problems of interdiffusion and defect concentration in the semiconductor. For dialkyltellurides, the rate of thermal decomposition increases in the order $Me_2Te > Et_2Te > {}^{i}Pr_2Te > {}^{t}Bu_2Te$.

The decrease in decomposition temperature can be rationalised by either (or both) a radical or β-hydrogen elimination mechanism(s). In both mechanisms cleavage of the first Te–C bond is assumed to be the rate determining step; the molecular fragment formed ($RTe^{\bullet}$ or RTeH) is believed to be inherently unstable, undergoing rapid decomposition to give tellurium metal and a hydrocarbon. This implies that any potential tellurium precursors require only one easily cleaved Te–C bond as any molecular fragment formed would rapidly decompose to give tellurium metal.

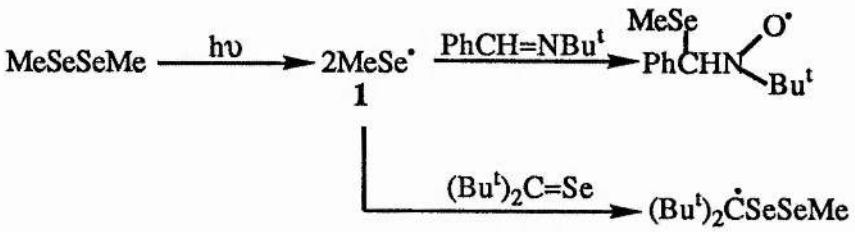
Homolysis of the Te–C bond should give a Te centred radical, of which there are only brief reports in the literature.

6.2 A Comparison With Organoselenium Radicals.

The absence of information about tellurium radicals prompts a comparison with selenium centred radicals which may be expected to behave in a similar way.

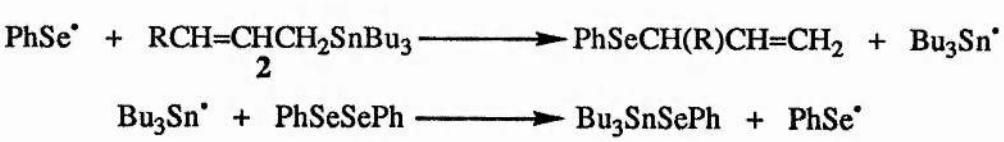
6.2.1 Diselenides.

Photolysis of diselenides is known to produce selenyl radicals. Photolysis of a solution of dimethyldiselenide in the cavity of an ESR spectrometer failed to show the methylselenyl radical, **1**, but in the presence of a nitrone spin trap or di-*tert*-butyl-selenoketone, trapped adducts of **1** were easily detected.[229]



Nitrosodurene has been used to spin trap arylselenyl radicals from the photolytic scission of diphenyldiselenides.[230]

Photolysis of diphenyldiselenide in the presence of allyltin derivatives, **2**, results in an addition-elimination reaction which occurs with high efficiency.[148] Propagation of the radical chain is achieved by S_H2 displacement of PhSe• from the diselenide by the displaced tin radical.

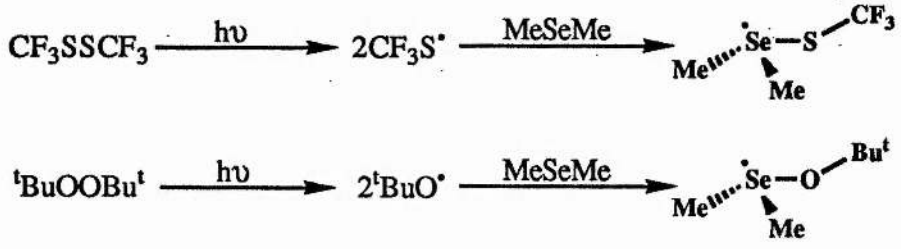


6.2.2 Organometallic-selenols.

Photoinitiated additions of Et_3M–SeH (M = Si or Ge) to a variety of alkenes has been achieved. The ease of oxidation of selenols has led to investigation of the use of these compounds as reducing agents. Diselenides are often produced in such reactions but there is no definite evidence for radical involvement.

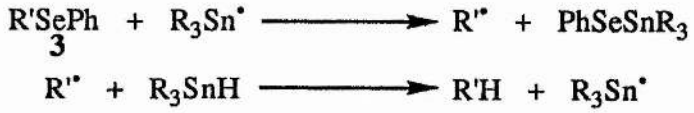
6.2.3 S_H2 Displacement.

Radical attack at selenium proceeds *via* a selenuranyl radical and in certain cases such species have been observed by ESR. Examples of this include the reaction of trifluoromethylthiyl and *tert*-butoxyl radicals.[231]

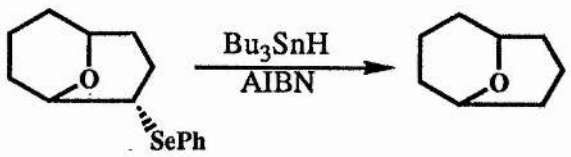


6.2.4 Reactions Of Monoselenides.

Reductive elimination using tin hydride is an important reaction in which alkyl phenyl selenides, **3**, are cleaved to give alkanes by a radical chain process.



An example of this reaction is;[232]

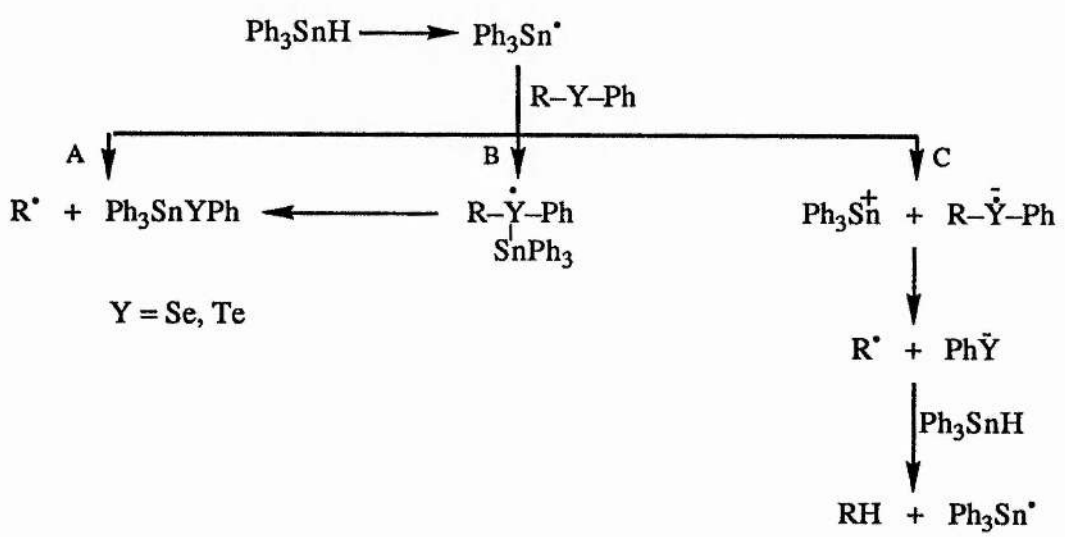


This reaction has been extended to the reduction of selenoketals, which affords a new alternative to the Wolff-Kishner reduction of carbonyl to methylene. It has been observed that the phenyltelluryl group may be removed in the same way. In the absence of AIBN, the reaction with tellurium compounds generally proceeds at lower temperatures (*ca.* 50 °C) than those of selenium analogues (*ca.* 100 °C), but the organotelluriums are very sensitive to photolysis.[233,234]

Phenyl alkyl tellurides, **4**, are reduced by triphenyltin hydride under mild conditions to give the corresponding hydrocarbons, **5**.

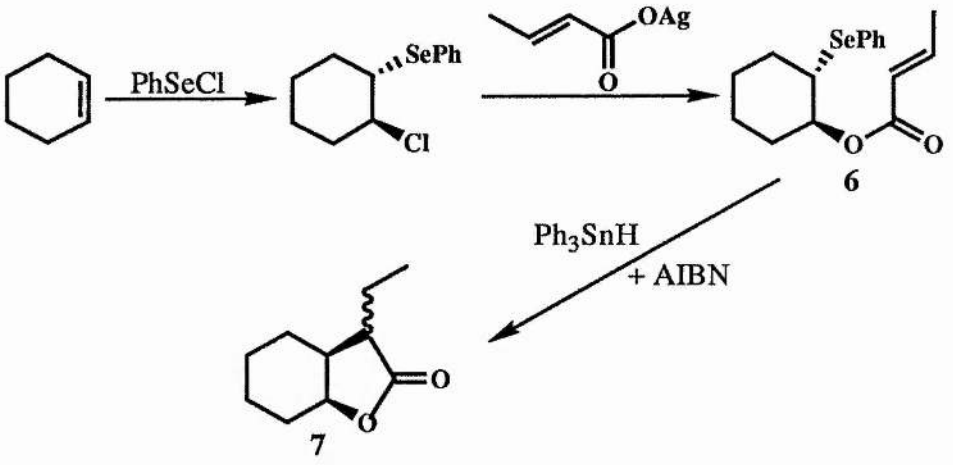
$$\underset{\mathbf{4}}{R\text{–}Te\text{–}C_6H_5} \xrightarrow{Ph_3SnH} \underset{\mathbf{5}}{RH} + Ph_3Sn\text{–}Te\text{–}C_6H_5$$

The precise mechanism of the reaction is uncertain, but it has been proposed that a direct or two-step radical displacement (path A or B) as well as an electron transfer sequence (path C) may be envisaged by analogy with the mechanism for the reduction of phenyl alkyl selenides.[234]



If path B operates then the intermediacy of a tellurium centred radical is involved.

Reduction of a selenide in the vicinity of a double bond has been used to bring about the intramolecular cyclisation of acrylate esters, **6**, to give lactones, **7**.[235]



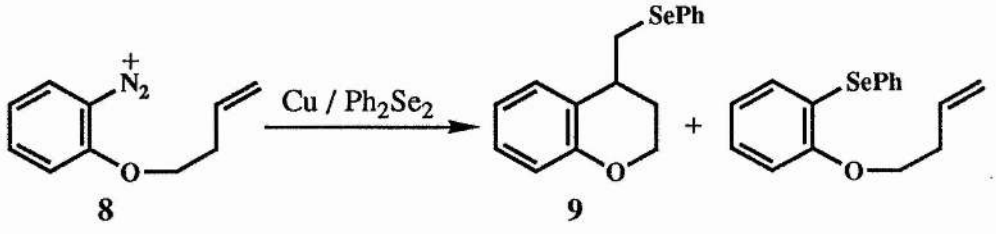
The success of the above reaction depends on the efficiency of the attack on selenium by the trialkyltin radicals and the mode of fragmentation of the intermediate selenuranyl radical. Estimates of the rates of such S_H2 displacements by $Bu_3Sn^{\bullet}$ have shown the order of reactivity to be $Me_2Te > Me_2Se > Me_2S$.[236]

6.2.5 Reactions Of Diselenides.

S_H2 reaction of diselenides leads to selenium containing products.

$$R'^{\bullet} + RSeSeR \longrightarrow R'SeR + RSe^{\bullet}$$

Efficient synthesis of unsymmetrical diaryl diselenides using copper catalysed decomposition of the corresponding diazonium salt has been carried out in the presence of diphenyl diselenide. If a neighbouring double bond is present, as in **8**, the aryl radical intermediate may be intercepted to give a cyclic product, **9**.[237]



8 **9**

The rate of reaction of diphenyl diselenide with primary alkyl radicals has been studied[238,239] using the hex-5-enyl radical 'clock'. It was shown that the reaction proceeds more efficiently with diphenyl diselenide and diphenyl ditelluride than with diphenyl disulphide which is significantly slower.

6.2.6 α-Selenoalkyl Radicals.

Hydrogen abstraction by *tert*-butoxyl radicals from dimethyl diselenide is easier than from saturated alkanes, yet the α-selenoalkyl radicals are undetectable by ESR.[229] This has been attributed to strong electron interaction with the selenium lone pair, resulting in line broadening by both spin rotation and spin-orbit mechanisms. In contrast, sterically hindered selenoalkyl radicals are observable by ESR as the steric constraints force them to adopt a geometry in which there is little interaction between the unpaired electron and the selenium electrons. An example of this type of radical has been observed as a result of addition to the selenium atom of di-*tert*-butylselenoketone, **10**.[229,240]

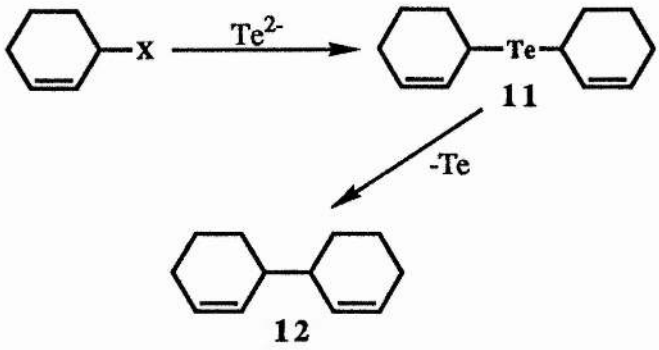
$$R_nM^{\bullet} + Se{=}CBu^t_2 \longrightarrow \underset{\mathbf{10}}{R_nMSe\dot{C}Bu^t_2}$$

6.2.7 Selenosulphonylation Of Alkenes.

β-Selenosulphones are formed in the free radical addition of phenylareneselenosulphonates to alkenes. Examples of this type of reaction are shown in § 3.8.

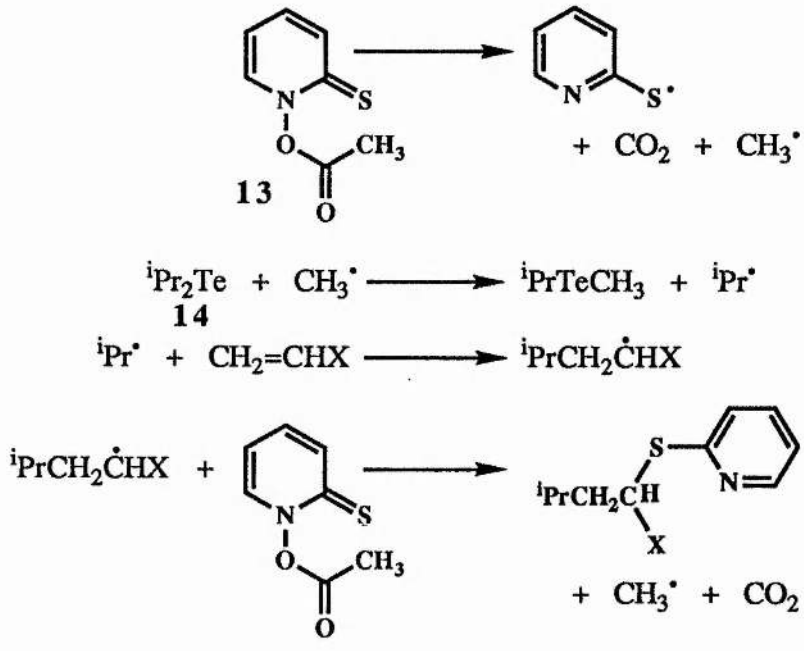
6.3 Organotellurium Compounds In Radical Reactions.

Alkyl halides have been found to react with telluride anions to give coupled allylic products.



Whilst the intermediate bis-3-cyclohexenyl telluride, **11**, has been observed by NMR, it decomposes rapidly in solution by extrusion of elemental tellurium. The resulting cyclohexenyl radicals simultaneously formed in this decomposition recombine to give bis(cyclohexenyl), **12**.[237,241,242]

Primary carbon radicals generated by photolysis of *N*-hydroxypyridine-2-thione, **13**, have been shown to displace *iso*-propyl radicals from di-*iso*-propyltelluride, **14**, which subsequently go on to react with alkenes.[243]



This type of displacement is not limited to *iso*-propyltellurides, but has been carried out using anisyltellurides as well.[244]

6.4 Tellurium Centred Free Radicals.

Whilst no tellurium centred radical has ever been reported to have been observed by ESR, they have been detected using laser photoinitiation time-of-flight mass spectrometry from UV excimer laser irradiation of gaseous dimethyltelluride, diethyltelluride and dimethylditelluride. Photofragments formed by excimer laser irradiation (ArF (193 nm), KrF (248 nm) and XeCl (308 nm)) revealed the following species.[245]

Organotellurium	Photofragment
$Te(CH_3)_2$	C, CH_3, Te, $TeCH_3$
$Te(C_2H_5)_2$	Te
$(TeCH_3)_2$	CH_3, Te, Te_2, $TeCH_3$

Chapter Seven

Organotellurium Compounds As Free Radical Precursors.

Since so little is known about the mode of decomposition of organotellurium compounds, an ESR study was carried out in order to attempt to observe any radical species formed.

7.1 Symmetrical Dialkyltellurides.

7.1.1 Thermolysis.

Heating degassed solutions of dialkyltellurides, R_2Te up to 90 °C in *tert*-butylbenzene did not give detectable signals from either alkyl or tellurium based radicals. However, decomposition of the telluride within this temperature region normally occurred because deposition of a tellurium mirror was observed. Deposition of tellurium was observed when R = ^{i}Pr, ^{t}Bu and allyl, but did not occur for R = Me. In the MOVPE process, dimethyltelluride requires much higher decomposition temperatures compared to the *iso*-propyl and *tert*-butyl analogues, probably due to a particularly strong C–Te bond strength in Me_2Te. A driving force for bond breakage would be the formation of a free radical and formation of a tertiary radical (^{t}Bu$^{\bullet}$) is strongly favoured over formation of a methyl radical.

7.1.2 Photolysis.

Photolysis of degassed solutions of dialkyltellurides in *tert*-butylbenzene again resulted in the deposition of elemental tellurium. However, with di-*tert*-butyltelluride and diallyltelluride, the corresponding *tert*-butyl and allyl radicals were observed. In the case of the allyl compound, very good, strong spectra were obtained, but over a period of time the signal became affected by the build up of metallic tellurium on the walls of the sample tube.

Radical	h.f.s/G	Literature g-value	h.f.s/G
tert-butyl	a(9H) 22.7	2.00276	a(9H) 22.73 [246]
allyl	$a(H_{1,3\text{-}exo})$ 14.8, $a(H_{1,3\text{-}endo})$ 14.1 $a(H_2)$ 4.2	2.0026	$a(H_{1,3\text{-}exo})$ 14.8, $a(H_{1,3\text{-}endo})$, 14.0 $a(H_2)$4.53 [192]

The *iso*-propyl radical was not observed in the case of di-*iso*-propyltelluride, however, a tellurium mirror was deposited which suggested a reaction was occurring.

$$R_2Te \xrightarrow{h\upsilon} R^{\bullet} + RTe^{\bullet}$$

$$R^{\bullet} + RTe^{\bullet} \longrightarrow Te + R^{\bullet}$$

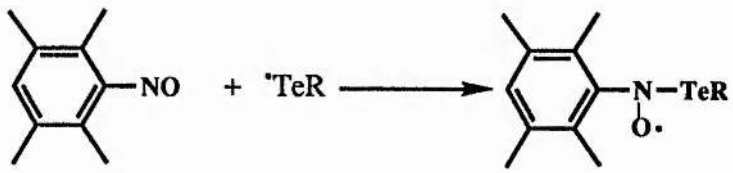
$R = {}^{i}Pr, {}^{t}Bu$, allyl

As before, no signal or tellurium deposition was observed with dimethyltellurium. Presumably a tellurium centred radical, $RTe^{\bullet}$, must accompany the formation of $R^{\bullet}$ but it is too transient or its signal is too broad for it to be observed by ESR. It may be that tellurium centred free radicals could be observed if they were 'isolated' by using some solvent other than a hydrocarbon. Use of liquid xenon has been employed as a solvent for ESR studies[247] and its inertness may provide a suitable medium for which to try and observe these highly transient tellurium-centred radicals directly.

7.1.3 Spin Trapping.

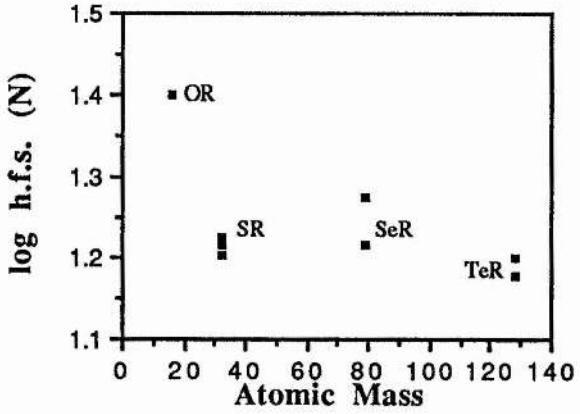
Spin trapped *iso*-propyl, *tert*-butyl and allyl radicals were observed when the corresponding dialkyltellurides were heated in the presence of nitrosodurene.

In the case of di-*iso*-propyltelluride and di-*tert*-butyltelluride a second radical was also trapped, which it is believed may be a tellurium centred radical, $RTe^{\bullet}$.



R	g-value	h.f.s/G	Literature g-value	Literature h.f.s/G
Pr^i		*a*(N) 13.6, *a*(1H) 6.5	2.0061	*a*(N) 13.72, *a*(1H) 6.92 [20]
Bu^t		*a*(N) 13.8	2.0060	*a*(N) 13.60 [20]
allyl		*a*(N) 13.5, *a*(2H) 10.3	2.0060	*a*(N) 13.57, *a*(2H) 10.20 [96]
$TePr^i$	2.0079	*a*(N) 14.9		
$TeBu^t$	2.0060	*a*(N) 15.6		

That it is a tellurium centred radical was deduced from the fact that three lines were observed in the spectrum and that the magnitude of the hyperfine splittings were of a reasonable order when compared to other nitrosodurene spin trapped group VI atom centred radicals. A plot of $\log_{10}$ (h.f.s.) *versus* the atomic mass of the group VI element shows how they decrease in decending the group.



Thermal instability may present a problem with the long-term storage of organotellurium compounds. Strong spectra of the trapped allyl radical were observed at room temperature for diallyltelluride, allylmethyltelluride and strong spectra of the trapped *tert*-butyl radical were observed at room temperature for di-*tert*-butyltelluride, *tert*-butylmethyltelluride and di-*tert*-butylditelluride, which shows that decomposition is occurring without heating these compounds. In the case of di-*iso*-propyltelluride the

decomposition temperature was higher than for the allyl and *tert*-butyl compounds. Whilst the trapped *iso*-propyl radical was observed at room temperature it was lower in concentration than the trapped allyl and *tert*-butyl radicals. Increasing the temperature of the sample resulted in the rapid onset of thermal decomposition occurring at *ca.* 320-330 K which was observed as a sudden increase in the concentration of the trapped *iso*-propyl radical.

7.1.4 Reaction With *tert*-Butoxyl Radicals

Photolysis of solutions of dialkyltellurides containing di-*tert*-butyl peroxide gave exactly the same results as photolysis in the absence of peroxide. This may be because (i) the dialkyltelluride photolytically decomposes before the *tert*-butoxyl radicals react with it, (ii) *tert*-butoxyl radicals do not react with the dialkyltellurides or (iii) hydrogen abstraction does occur but the α-telluroalkyl radical formed is not detectable by ESR. The detection of α-selenoalkyl radicals by ESR has not proved possible without the presence of a spin trapping agent (see § 6.2.6).

7.2 Unsymmetrical Dialkyltellurides.

Organotelluriums of the type RTeMe, it has been proposed, should have the best combination of volatility and decomposition characteristics and growth studies using allylmethyltelluride have confirmed this.[248]

tert-Butylmethyltelluride and allylmethyltelluride were both studied by ESR. In each case they behaved in exactly the same manner as di-*tert*-butyltelluride and diallyltelluride respectively. The fact that these alkylmethyltellurides decompose readily suggests that only one Te–C bond needs to be readily cleaved for tellurium deposition to occur and hence their high volatility and low decomposition temperatures make them ideal precursors for low temperature growth of tellurium containing semiconductors.

7.3 Dialkylditellurides.

7.3.1 Thermolysis.

Thermolysis of dimethylditelluride both with and without a nitrosodurene spin trap failed to produce any observable radicals by ESR in the accessible temperature range. Thermolysis of di-*tert*-butylditelluride did, however, give rise to a spectrum of the spin trapped *tert*-butyl radical.

7.3.2 Photolysis.

On photolysis of dimethylditelluride, no signal was observed by ESR, but a tellurium mirror was deposited.These observations may be explained by initial extrusion of one tellurium atom to give the monotelluride, which then behaves as described earlier.

$$RTeTeR \xrightarrow{\Delta \text{ or } h\upsilon} RTeR + Te \quad (1)$$

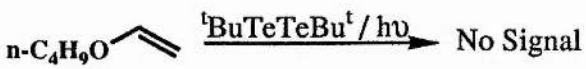
$$RTeR \xrightarrow{\Delta \text{ or } h\upsilon} RTe^{\bullet} + R^{\bullet} \quad (2)$$

When R = CH_3 the reaction ceases after step (1), whilst when R = Bu^t, it carries on to step (2) and the *tert*-butyl radical is observed (with the aid of a spin trap). With di-*tert*-butylditelluride, no signal was observed on direct photolysis, but a tellurium mirror was observed. A short irradiation of the sample with UV light in the presence of a spin trap did give a spectrum of the trapped *tert*-butyl radical.

7.4 Radical Reactions Using Dialkylditellurides.

It was attempted to react the *tert*-butyltelluryl radical generated from di-*tert*-butylditelluride with an alkene.

A mixture of di-*tert*-butylditelluride and *n*-butyl vinyl ether were photolysed in the cavity of an ESR spectrometer. Whilst elemental tellurium deposition occurred, no adduct radicals were observed.



It may be that a large enough concentration of the *tert*-butyltelluryl radical was never reached for a detectable level to be observed. It would be interesting to observe whether the organotellurium could be used as a source of *tert*-butyl radicals, which could then react with an electron deficient alkene to form a new adduct radical. Unfortunately, due to problems with the ESR cavity and lack of time available it has not been possible to repeat this experiment using an alkene containing an electron withdrawing substituent.

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